Syntheses of copper(I) *cis*-1,3,5-tri-iminocyclohexane complexes†

Alison K. Nairn, Stephen J. Archibald, Rajiv Bhalla, Clive J. Boxwell, Adrian C. Whitwood and Paul H. Walton*

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Copper(I) complexes of the ligand *cis*-1,3,5-tris(cinnamylideneamino)cyclohexane (**L**) have been prepared from a versatile precursor complex, $[Cu^{I}(\mathbf{L})NCMe]BF_4$, which incorporates a labile acetonitrile ligand that can be exchanged to give a range of new Cu(**L**)X complexes (where X = Cl, Br, NO_2, SPh). ^{1}H NMR spectra and X-ray structures of the Cl, Br and NO_2 complexes show **L** coordinated in a symmetric fashion about the copper centre. The complexes have been further characterised using UV/Visible spectroscopy and cyclic voltammetry. Cu**L**Cl shows an electrochemically reversible $Cu^{I/II}$ redox couple at 0.51 V (*vs.* Ag/AgCl) while the Cu**L**NO_2 complex shows an analogous quasi-reversible wave at 0.41 V (*vs.* Ag/AgCl).

Introduction

We recently reported the use of *cis*-1,3,5-tri-iminocyclohexane-based ligands and their complexes as models of metalloenzyme active sites.[1,2] This ligand system provides a face-capping N_3 coordination environment around the metal ion and can also be readily derivatised to model features of an active site which are remote from the immediate metal coordination sphere. Modelling remote interactions has been highlighted as of importance in the synthesis of more effective biomimetic complexes.[3–7] It is in this respect that we report here the syntheses and characterisations of a range of new copper complexes with tri-iminocyclohexane-based ligands. Despite their biomimetic potential, particularly in modelling Type 1 and Type II copper sites,[8] copper complexes of this ligand system are uncommon.[9] The closest related examples are copper complexes of tri-hydroxy-tri-aminocyclohexane and of tri-aminocyclohexane itself, which are of some interest as they are known to be effective catalysts in the hydrolysis of DNA.[10]

Results and discussion

The ligand *cis*-1,3,5-tris-(cinannamylideneamino)cyclohexane (**L**) was prepared as reported previously.[1] Direct reaction of (**L**) with $[Cu(NCCH_3)_4]BF_4$ in CH_2Cl_2 gives $[Cu(\mathbf{L})NCCH_3]BF_4$ (**1**) (Fig. 1) in 46% yield as an intense yellow-coloured powder, and was characterised by ^{1}H-NMR, MS and elemental analysis. **1** is mildly air sensitive; exposure to air results in a gradual colour change from intense yellow to green, presumably due to the formation of the corresponding copper(II) complex.

1 is a versatile starting point for the preparation of a number of different complexes. The acetonitrile ligand is labile and can be readily exchanged with other ligands. For example, reaction of **1** with $[NEt_4]Cl$ in CH_2Cl_2 gives Cu(**L**)Cl (**2**) in 45% yield, and reaction with $[NEt_4]Br$ gives Cu(**L**)Br (**2a**) in 86% yield (Fig. 1). A colour change from intense yellow to intense dark red is observed in each of the complexation reactions. **2** can be prepared by the direct addition of **L** to Cu(I)Cl, and can also be prepared from the corresponding copper(II) complex (prepared from addition of **L** to $Cu(II)Cl_2{\cdot}nH_2O$) by adding a mild reducing agent such as $NaBPh_4$. **2** is EPR silent and appears to be air-stable.

2 and **2a** are crystallised by layering a CH_2Cl_2 solution of the complex with either hexane or cyclohexane to give large dark red blocks. The X-ray structure shows the copper(I) centre in a C_{3v} coordination environment with the halide in the axial position and **L** coordinating in the expected N_3 face-capping fashion, with the cinnamyl 'arms' of **L** forming a stereochemically rigid cavity around the chloride. For **2**, the Cu–N distances are in the range

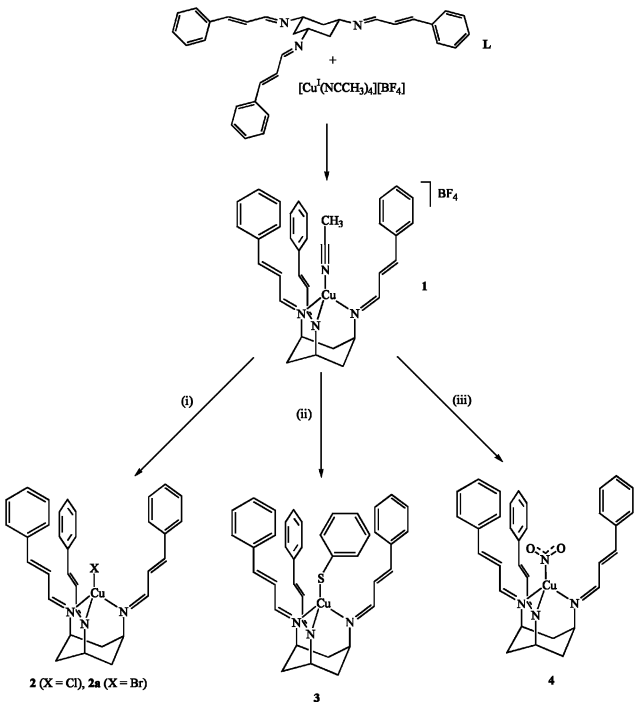

Fig. 1 Preparation of $[Cu(\mathbf{L})NCCH_3]BF_4$ complex (**1**) and ligand exchange reactions of **1**, (i) $[NEt_4]X$, X = Cl or Br; (ii) NaSPh; (iii) $[NBu_4]NO_2$.

Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: phw2@york.ac.uk; Fax: +44 1904 432516; Tel: +44 1904 432500

† Electronic supplementary information (ESI) available: ORTEP diagram and NMR spectrum of **2a**; NMR of aliphatic region of **3**; labelling of protons and carbons for assignment of NMR spectra of **1**, **2**, **2a**, **3** and **4**. See DOI: 10.1039/b510703b

of 2.077 Å to 2.086 Å, and the Cu–Cl distance is 2.285(3) Å. The N–Cu–N angles range from 91.4–96.8° and the N–Cu–Cl angles are in the range 120.6–124.3° (Fig. 2), structural details for **2a** can be found in the ESI (Fig. S1†).

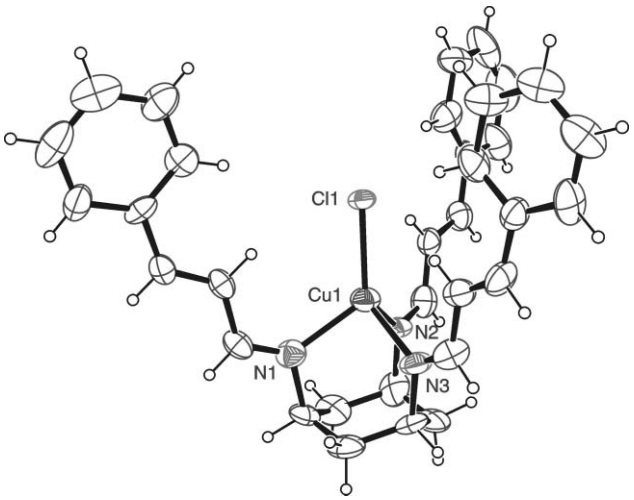

Fig. 2 ORTEP[11] (50% probability ellipsoids) representation of the Cu(**L**)Cl complex, **2**. Selected bond distances (Å) and angles (°): Cu–N(1) 2.077(9), Cu–N(2) 2.077(10), Cu–N(3) 2.086(9), Cu–Cl 2.285(3); N(1)–Cu–N(2) 91.4(4), N(1)–Cu–N(3) 96.8(4), N(2)–Cu–N(3) 93.1, N(1)–Cu–Cl 122.8(3), N(2)–Cu–Cl 124.3(3), N(3)–Cu–Cl 120.6(3).

The ^{1}H-NMR spectra of **2** and **2a** confirm the threefold symmetry of the complexes on the NMR time scale. Apart from very slight differences in the chemical shift of the signals the only difference seen between the spectra of the complexes is that the signal for the proton of the N=CH group, which is a sharp doublet in the chloride complex and is a broad singlet in the spectrum of the bromide complex (Fig. S2†).

The unusual intense red colours of **2** and **2a** are presumably due to the presence of the cinnamyl groups. The UV/Visible spectrum of **2** was recorded in CH_2Cl_2 and it shows four bands in the near UV and UV regions. Three bands at 227 nm (ε = 2000 dm^3 mol^{-1} cm^{-1}), 280 nm (ε = 66000 dm^3 mol^{-1} cm^{-1}), and 345 nm (ε = 13000 dm^3 mol^{-1} cm^{-1}) are assigned as π–π* transitions on the cinnamyl group of the ligand and a less intense band at 436 nm (ε = 2300 dm^3 mol^{-1} cm^{-1}) is tentatively assigned as an MLCT band. The free ligand shows π–π* transitions at 227 nm (ε = 58300 dm^3 mol^{-1} cm^{-1}) and 287 nm (ε = 74800 dm^3 mol^{-1} cm^{-1}), and there is a shoulder on this second band at 304 nm (ε = 46700 dm^3 mol^{-1} cm^{-1}). **2a** shows analogous bands at 229 nm (ε = 52500 dm^3 mol^{-1} cm^{-1}), 278 nm (ε = 123700 dm^3 mol^{-1} cm^{-1}), 344 nm (ε = 21200 dm^3 mol^{-1} cm^{-1}) and 436 nm (shoulder, ε = 3900 dm^3 mol^{-1} cm^{-1}) which are assigned as for **2**.

The cyclic voltammogram of **2** (Fig. 3), recorded in CH_2Cl_2, shows one clear process in the positive region at $E_{\frac{1}{2}}$ = 0.51 V *vs.* Ag/AgCl (ΔE = 100 mV, −0.04 V *vs.* $FeCp_2^+/FeCp_2$, i^{ox}/i^{red} = 1.00). The process is assigned to a reversible copper(I/II) redox couple. The CV of **2a** also shows a process in the positive region at $E_{\frac{1}{2}}$ = 0.57 V *vs.* Ag/AgCl, 0.02 V *vs.* $FeCp_2^+/FeCp_2$), however, this is not reversible (ΔE increases as the scan rate, v, is increased, and a plot of i^{ox} or i^{red} against $v^{\frac{1}{2}}$ is not linear).

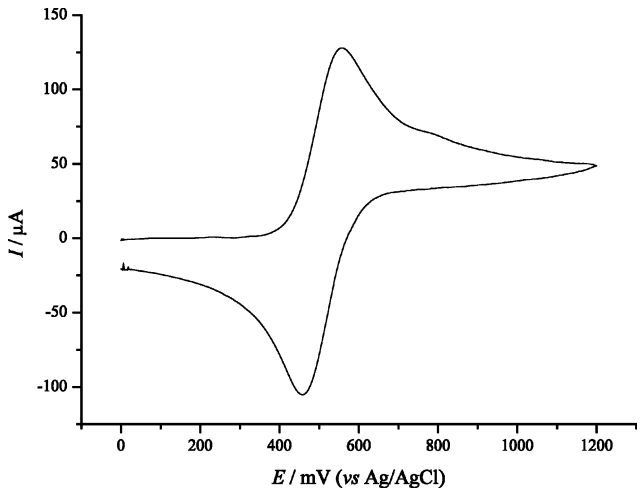

Fig. 3 Cyclic voltammogram of **2** in CH_2Cl_2 solution at 293 K.

Reaction of **1** with sodium thiophenolate in acetonitrile resulted in the synthesis of a new complex [Cu(**L**)(S–Ph)] (**3**), the formulation of which is suggested from ^{1}H-NMR, elemental analysis and MS. The NMR of the complex indicates that the ligand has two imine groups which are equivalent and one which is different, suggesting that the C_6H_5 group on the thiophenolate is placed between two of the cinnamyl rings and therefore gives an overall C_S symmetry. This structure is analogous to that of [Co(**L**)(O–Ph)]$^+$.[12] The protons on the cyclohexyl group also show the same inequivalence (Fig. S3†). **3** was studied by UV/Visible spectroscopy showing three bands at 224 nm (ε = 38200 dm^3 mol^{-1} cm^{-1}), 278 nm (ε = 54100 dm^3 mol^{-1} cm^{-1}) and 309 (shoulder, ε = 39500 dm^3 mol^{-1} cm^{-1}) which are assigned to the π–π* transitions of **L** (in reference to **2**). A fourth band is observed at 360 nm (a shoulder on the intense feature at 278 nm, ε = 5800 dm^3 mol^{-1} cm^{-1}).

The CuN_3S coordination sphere in **3** finds parallels in some Type-I copper redox-active proteins.[8] The redox activity of **3** was, therefore, investigated. The CV of **3** in CH_2Cl_2 shows three oxidative processes in the positive region (at E = 0.29, 0.62 and 0.89 V *vs.* Ag/AgCl) and one reductive process (E = 0.71 V *vs.* Ag/AgCl). No processes were observed in the negative region of the CV. The oxidative processes at 0.29 and 0.62 V are irreversible on the CV timescale. The third oxidation process at 0.89 V, however, does have a corresponding reductive wave, although the process is, at best, only pseudo-reversible ($E_{\frac{1}{2}}$ = 0.76 V *vs.* Ag/AgCl, 0.21 V *vs.* $FeCp_2^+/FeCp_2$, ΔE = 180 mV). This process is tentatively assigned as a copper(I/II) couple by reference to **2**. The oxidative processes at 0.29 and 0.62 V observed in the CV of **3** are difficult to assign, although it is likely that they are thiophenolate-based. Possible explanations include the oxidation of the thiophenolate to give the corresponding thiyl-radical species. This oxidation is unlikely to be reversible as formation of disulfide bonds would be very rapid.[13]

Reaction of **1** with $[Bu_4N][NO_2]$ in CH_2Cl_2 resulted in the synthesis of [Cu(**L**)(NO_2)] (**4**). **4** was studied by UV/Visible spectroscopy showing three bands at 230 nm (ε = 57600 dm^3 mol^{-1} cm^{-1}), 276 nm (ε = 122200 dm^3 mol^{-1} cm^{-1}) and 324 nm (shoulder, ε = 34600 dm^3 mol^{-1} cm^{-1}) which are assigned to the π–π* transitions of **L** (in reference to **2**). A fourth

band is observed at 390 nm (a shoulder on the intense feature at 276 nm, $\varepsilon = 6100$ dm^3 mol^{-1} cm^{-1}). The CV of the complex recorded in CH_2Cl_2, shows one pseudo-reversible wave in the positive region at $E_{\frac{1}{2}} = 0.41$ V *vs.* Ag/AgCl ($\Delta E = 100$ mV, −0.14 V *vs.* $FeCp_2^+/FeCp_2$, $i^{ox}/i^{red} = 1.00$). This is assigned to a $Cu^{I/II}$ redox couple in reference to **2**. As was seen in the CV for **2a**, the plot of i^{ox} against $v^{\frac{1}{2}}$ is not linear.

Crystals of **4** suitable for X-ray diffraction were grown from CH_2Cl_2/Et_2O solution. The structure of **4** is analogous to that of **2**, with a nitrite anion in place of the chloride (see Fig. 4 for ORTEP[11] depiction). The nitrite, as expected, is coordinated to the copper(I) as the nitro linkage isomer, similar to other copper(I)-nitrite complexes.[14] The Cu–N distances for **L** are in the range of 2.046 Å to 2.095 Å, and the Cu–N distance to the nitrite ligand is 2.006(1) Å. The N–Cu–N angles range from 91.9–94.4° and the N–Cu–NO_2 angles are in the range 120.0–125.8° (Fig. 4). Of note is the slightly unsymmetrical coordination mode of the nitrite anion which displays Cu···O distances of 2.781(1) and 2.883(1) Å. This slight distortion is presumably a result of the steric bulk of **L** affecting the possible coordination modes of the nitrite. Indeed, there is a very short O···H–C contact of 2.30(1) Å (N···C distance of 3.25(1) Å) between one nitrite oxygen atom and the central C–H of the propenyl unit of one of the cinnamyl groups.

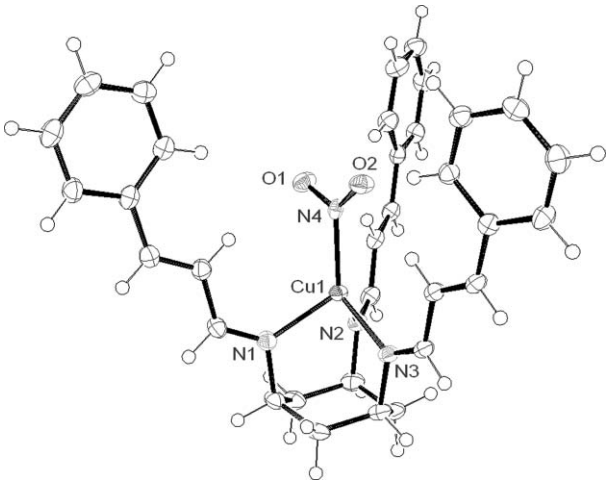

Fig. 4 ORTEP[11] (50% probability ellipsoids) depiction of **4**. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 2.0459(13), Cu(1)–N(2) 2.0644(13), Cu(1)–N(3) 2.0952(11), Cu(1)–N(4) 2.0059(12), N(4)–O(1) 1.2412(15), N(4)–O(2) 1.2185(15); N(1)–Cu(1)–N(2) 94.39(5), N(1)–Cu(1)–N(3) 91.85(5), N(2)–Cu(1)–N(3) 93.86(5), N(4)–Cu(1)–N(1) 119.96(5), N(4)–Cu(1)–N(2) 122.73(5), N(4)–Cu(1)–N(3) 125.76(5), O(1)–N(4)–Cu(1) 115.87(9), O(2)–N(4)–Cu(1) 124.98(9), O(2)–N(4)–O(1) 119.09(12).

The NMR spectrum of the complex, as for complexes **2** and **2a**, confirms the overall threefold symmetry of the complex as all three of the imine groups are equivalent on the NMR time scale. The crystal structure of the active site of the Type-II copper site of the nitrite form of *copper nitrite reductase* shows nitrito coordination,[15,16] an analogous CuN_3–NO_2 coordination geometry is seen in several examples of copper(II) model complexes.[14,17]

There are several related systems in the literature that have been prepared which incorporate a N_3 face-capping environment for a Cu^I centre, including several examples based on tris-pyrazoylborate.[18–22] Complexes of this type have commonly been employed as precursors in the preparation of nitrosyl adducts (Cu–NO), which are of key importance in both biological (*copper nitrite reductase*) and also certain catalytic processes.[20] However, preparation of such species is not as simple as the preparation of **L**; this ligand system can be readily varied, simply by changing the aldehyde employed in the ligand preparation reaction.[23–26] The imidazole derivatised calixarene system developed by Reinaud *et al.* shows the same C_{3v} symmetry about the copper centre as seen in complexes **1**, **2**, **2a** and **4**.[27–30] These complexes also incorporate a labile bound acetonitrile ligand. Like the [Cu(**L**)X] system, the ligand constrains the Cu^I centre in a tetrahedral environment and provides a hydrophobic cavity around the axial coordination site, therefore providing a means of stabilising the Cu^I state.[27]

Conclusions

Addition of tris(cinnamylideneamino)cyclohexane (**L**) to [Cu-$(CH_3CN)_4$]BF_4 gives a new copper(I) complex, [Cu(**L**)$NCCH_3$]-BF_4, which is a versatile precursor complex for the synthesis of [Cu(**L**)X] complexes. We have demonstrated the syntheses of a small range of such complexes with X = Cl^-, Br^-, ^-SPh or NO_2^- anions.

The chloride complex is air-stable, showing no oxidation to the corresponding copper(II) species over a period of several weeks. The complex exhibits an electrochemically reversible copper(I/II) redox couple at $E_{\frac{1}{2}} = 0.51$ V *vs.* Ag/AgCl ($\Delta E = 100$ mV). The corresponding bromide complex also shows a copper(I/II) redox couple at $E_{\frac{1}{2}} = 0.57$ V *vs.* Ag/AgCl but this is not electrochemically reversible. The analogous thiophenolate complex shows redox processes. An equivalent, but distinctly less reversible, copper(I/II) process is seen at $E_{\frac{1}{2}} = 0.73$ V *vs.* Ag/AgCl ($\Delta E = 140$ mV); this complex also exhibits other oxidative processes which are possibly due to oxidation of the thiophenolate.

Where X = NO_2^- the resulting complex shows nitrite in a nitro coordination mode. This complex exhibits a quasi-reversible $Cu^{I/II}$ redox couple like that seen in **2** at 0.41 V *vs.* Ag/AgCl ($\Delta E =$ 100 mV). Our future work will concentrate on characterising the complex redox processes of **3** and **4** and on investigating the biomimetic potential of the complexes.

Experimental

General methods

Solvents for synthesis were supplied by Fisons Ltd., or Fischer Scientific International Company. Deuterated solvents were supplied by Aldrich Chemical company. All other reagents were supplied by either Aldrich Chemical Company Ltd., Lancaster Chemicals Ltd., Avocado Research Chemicals Ltd. or Fluka Ltd. All the reagents were used without further purification, apart from all solvents which were dried over Na (Et_2O, hexane, cyclohexane) or CaH (CH_2Cl_2, CH_3CN) and then thoroughly degassed before use.

FT-NMR spectra were recorded using a Bruker AV500 500 MHz spectrometer, referencing of the peaks was carried out using the residual protons in the solvent. For an explanation of signal assignments see Fig. S4.† Infrared spectra were recorded using a Mattson Sirius Research Series FTIR Spectrometer as KBr discs

(pressed under 7 tonnes pressure). Mass spectra were recorded on a Fisons Instruments Autospec. using a 0 to 650 °C temperature range. Elemental analyses were performed at the micro analytical laboratory at the University of Manchester. UV/Visible spectra were recorded on a Hitachi U-3000 spectrometer using 1 cm path length quartz cells.

Cyclic voltammetry was performed using a standard three-electrode configuration with platinum working (0.5 mm diameter disk) and counter electrodes and a Ag/AgCl reference which gave the $FeCp^+/FeCp$ couple at 0.55 V ($\Delta E = 80$ mV) using an EG & G potentiostat. All measurements were made in a nitrogen-purged solution of CH_2Cl_2–0.5 mol dm^{-3} [n-Bu_4N][BF_4] over a range of scan rates (from 50 to 500 mV s^{-1}). All the data obtained from the electrochemical and UV/Visible studies were processed using the Origin software package for Microsoft Windows (version 6.0).

Crystallography

Diffraction data for **2** were measured using a MSC Rigaku AFC6S diffractometer (Mo-K_α radiation, $\lambda = 0.71069$ Å). TeXsan (single crystal analysis software) was used as an interface to the solution software.[31] The structure was solved by Patterson Methods using DIRDIF94 and expanded using Fourier techniques with DIRDIF.[32] The structure was refined using full matrix least-squares on F^2 with SHELXL-97.[33] All non-hydrogen atoms of the complex molecule cations and the associated anions were refined anisotropically. Hydrogen atoms were refined using a rigid model.

Diffraction data for **2a** and **4** were collected at 100(2) K on a Bruker Smart Apex diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using SMART.[34] Frame integration and unit-cell refinement software was carried out with SAINT+.[35] Absorption corrections were applied by SADABS.[36] Structures were solved by direct methods using SHELXS-97[37] and refined by full-matrix least squares using SHELXL-97.[33] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

Crystal structure analysis for 2. $C_{33}H_{33}ClCuN_3$, $M = 570.61$, dark red block, crystal dimensions 0.60 × 0.40 × 0.30 mm, orthorhombic, $a = 21.873(7)$, $b = 22.840(4)$, $c = 12.268(7)$ Å, cell volume = 6129(4) Å^3, $T = 150(2)$ K, space group $Pbca$ (61), $Z = 8$, reflections measured = 4258, 4258 unique in the range $2.06 \leq \theta \leq 24.98$, $R1 = 0.0468$.

Crystal structure analysis for 2a. $C_{33}H_{33}BrCuN_3$, $M = 615.07$, dark red plates, crystal dimensions 0.24 × 0.11 × 0.03 mm, orthorhombic, $a = 12.957(3)$, $b = 21.405(5)$, $c = 21.458(5)$ Å, cell volume = 5951(2) Å^3, $T = 100(2)$ K, space group $Pca2_1$, $Z = 8$, reflections measured = 60979, 14757 unique in the range $0.95 \leq \theta \leq 28.33$, $R1 = 0.0416$.

Crystal structure analysis for 4. $C_{33}H_{33}CuN_4O_2$, $M = 581.17$, dark red block, crystal dimensions 0.23 × 0.17 × 0.17 mm, orthorhombic, $a = 12.2294(10)$, $b = 13.5896(11)$, $c = 17.0826(14)$ Å, cell volume = 2839.0(4) Å^3, $T = 100(2)$ K, space group $Pna2_1$, $Z = 4$, reflections measured = 39581, 7567 unique in the range $1.91 \leq \theta \leq 29.06$, $R1 = 0.0261$.

CCDC reference numbers 279581–279583.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510703b

Syntheses

Tris(cinnamlyideneamino)cyclohexane (**L**) was prepared following literature procedures.[1]

[Cu(L)NCCH$_3$]BF$_4$ (1). **L** (0.1006 g, 0.21 mmol) was placed in a Schlenk tube and dissolved in CH_2Cl_2 (5 ml) to give a colourless solution. $Cu^I(CH_3CN)_4(BF_4)$ (0.0668 g, 0.21 mmol) was placed in a second Schlenk tube and dissolved in dry degassed CH_2Cl_2 (5 mL) to give a colourless solution. The solution of the copper salt was transferred to the solution of the phenyl-protach ligand *via* cannula and an instantaneous colour change to intense yellow was observed. The solution was stirred for $\frac{1}{2}$ h and then filtered through Celite. The solvent was reduced to 1 mL and then Et_2O (10 mL) was added and the mixture stirred. A fine, bright yellow precipitate formed which was collected by filtration, washed with Et_2O (2 × 5 mL) and then dried (0.0657 g, 0.09 mmol, 46%). Elemental analysis: $C_{35}H_{36}N_4CuBF_4.0.5CH_2Cl_2$: calc C 60.44, H 5.29, N 7.94; found C 61.19 H 5.24, N 7.69%. ^{1}H NMR (CD_2Cl_2): δ 1.97 (d, 3H, *cis*-tachCH_2, H^B), 2.33 (d, 3H, *trans*-tachCH_2, H^A), 2.57 (s, broad, 3H, CH_3CN), 3.98 (s broad, 3H, tachCH, H^C), 7.21 (d, 6H, Ph–CH=CH–CH=, H^F and H^E), 7.47 (d of t, 9H, ArCH, H^H and H^I), 7.57 (d, 6H, ArCH, H^G), 8.03 (t, 3H, N=CH–CH, H^D). ^{13}C NMR (CD_2Cl_2): δ 37 (tach-CH$_2$, C1), 65 (tach-CH, C2), 126 (Ar–CH=CH, C5), 127 (ArCH, C8), 129 (ArCH, C7), 130 (ArCH, C9), 135 (ArC, C6), 144 (N=CH–CH=CH, C4), 162 (N=CH–CH C3). MS (ES): m/z 574 [^{63}Cu**L**(CH$_3$CN)$^+$ − H], 576 [^{65}Cu**L**(CH$_3$CN)$^+$ − H], 534 [^{63}Cu**L**$^+$], 536 [^{65}Cu**L**$^+$]. IR/cm^{-1} (KBr disk): 3559 (b, w), 3056 (w), 3023 (w), 2917 (m), 1626 (s, $\nu_{C=N}$), 1601 (m), 1491 (w), 1442 (m), 1397 (w), 1356 (w), 1295 (w), 1258 (w), 1164 (m), 1123 (m), 1058 (s), 976 (m), 911 (w), 886 (w), 747 (s), 678 (s), 547 (w), 502 (m).

[Cu(L)Cl] (2). ***Method 1.*** **L** (0.1030 g, 0.22 mmol) was dissolved in dry, degassed CH_2Cl_2 (10 ml) under argon in a Schlenk tube to give a yellow solution. CuCl (0.0231 g, 0.22 mmol) was placed in a Schlenk tube under argon. The solution of **L** was added *via* cannula to the metal salt to give an intense orange-coloured solution. The solution was degassed for 15 min and left to stir for 24 h after which it had become intense red in colour. The solution was layered with dry/degassed hexane (20 mL) and left to crystallise. After *ca.* 14 d, intensely red-coloured crystals had formed which were collected and dried under vacuum (0.0563 g, 0.10 mmol, 45%).

Method 2. **1** was prepared as before using **L** (0.1000 g, 0.21 mmol) and $Cu^I(MeCN)_4(BF_4)$ (0.0660 g, 0.21 mmol) in CH_2Cl_2 solution (10 mL). NEt_4Cl (0.0351 g, 0.21 mmol) was placed in a separate schlenk under N_2 and dissolved in dry, degassed CH_2Cl_2 to give a colourless solution. The NEt_4Cl solution was added *via* cannula to the bright yellow solution of **1** and an instantaneous colour change to intense orange/red was observed. The solution was stirred for $\frac{1}{2}$ h and then filtered to remove a fine precipitate. The volume of the solution was reduced to 2 mL and layered with hexane and then left to crystallise as for method 1 (0.0560 g, 0.10 mmol, 45%). Elemental analysis: $C_{33}H_{33}N_3CuCl$: calc C 69.70, H 5.85, N 7.40, found C 69.15, H 5.93, N 7.31%. ^{1}H NMR (CD_2Cl_2): δ 2.00 (d, 3H, *cis*-tachCH_2,

H^B), 2.29 (d, 3H, *trans*-tachCH_2, H^A), 3.91 (s broad, 3H, tachC*H*, H^C), 7.01 (d, 3H, Ph–C*H*=CH–CH=, H^F), 7.37 (t, 3H, ArC*H* H^I), 7.43 (t, 6H, ArC*H*, H^H), 7.74 (d, 6H, ArC*H*, H^G), 7.79 (d, 3H, N=C*H*–CH, H^D), 8.42 (d of d, 3H, N=CH–C*H*=CH, H^E). ^{13}C NMR (CD_2Cl_2): δ 38 (tach-*C*H_2, C1), 65 (tach-*C*H, C2), 127.5 (N=CH–*C*H=CH, C4), 128 (Ar*C*H, C8), 129 (Ar*C*H, C7), 129.5 (Ar*C*H, C9), 136 (Ar*C*, C6), 143 (Ar–*C*H=CH, C5), 161 (N=*C*H–CH C3). MS (ES): m/z = 534 [^{63}Cu**L**$^+$], 536 [^{65}Cu**L**$^+$]. IR/cm^{-1} (KBr pressed disk): 3048 (w), 3021 (w), 2993 (w), 2926 (m), 2907 (m), 2858 (m), 1631 (s, $\nu_{C=N}$), 1591 (m), 1441 (m), 1387 (w), 1270 (m), 1164 (m), 1128 (s), 996 (s), 918 (w), 896 (w), 747 (s), 687 (m), 556 (m).

[Cu(L)Br] (2a). **1** was prepared as before using **L** (0.1002 g, 0.21 mmol) and Cu^I(MeCN)$_4$(BF_4) (0.0666 mg, 0.21 mmol) in CH_2Cl_2 solution (10 mL). NEt_4Br (0.0454 g, 0.22 mmol) was placed in a separate Schlenk under N_2 and dissolved in dry, degassed CH_2Cl_2 to give a colourless solution. The NEt_4Br solution was added *via* cannula to the bright yellow solution of **1** and an instantaneous colour change to intense orange/red was observed. The solution was stirred for $\frac{1}{2}$ h and then filtered to remove a fine precipitate. The volume of the solution was reduced to 2 mL and layered with Et_2O and then left to crystallise. A week later dark red crystals had formed, these were collected by filtration, washed with Et_2O and then dried (0.1122 g, 0.18 mmol, 86%). Elemental analysis: $C_{33}H_{33}N_3CuBr$: calc C 64.44, H 5.41, N 6.83; found C 63.91, H 5.20, N 6.69%. ^{1}H NMR (CD_2Cl_2): δ 2.02 (d, 3H, *cis*-tachCH_2, H^B), 2.30 (d, 3H, *trans*-tachCH_2, H^A), 3.96 (s broad, 3H, tachC*H*, H^C), 7.01 (d, 3H, Ph–C*H*=CH–CH=, H^F), 7.37 (t, 3H, ArC*H* H^I), 7.44 (t, 6H, ArC*H*, H^H), 7.76 (d, 6H, ArC*H*, H^G), 8.04 (d, 3H, N=C*H*–CH, H^D), 8.53 (d of d, 3H, N=CH–C*H*=CH, H^E). ^{13}C NMR (CD_2Cl_2): δ 38 (tach-*C*H_2, C1), 66 (tach-*C*H, C2), 128 (N=CH–*C*H=CH, C4), 128.5 (Ar*C*H, C8), 129 (Ar*C*H, C7), 130 (Ar*C*H, C9), 136 (Ar*C*, C6), 143 (Ar–*C*H=CH, C5), 162 (N=*C*H–CH C3). MS (ES): m/z = 534 [^{63}Cu**L**$^+$], 536 [^{65}Cu**L**$^+$], 613 [^{63}Cu**L**^{79}Br$^+$], 615 [^{63}Cu**L**^{81}Br$^+$ and ^{65}Cu**L**^{79}Br$^+$], 617 [^{65}Cu**L**^{81}Br$^+$]. IR/cm^{-1} (KBr pressed disk): 3056 (w), 3011 (m), 2904 (w), 2852 (m), 1621 (s, $\nu_{C=N}$), 1593 (m), 1491 (w), 1450 (w), 1389 (w), 1352 (w), 1291 (w), 1258 (w), 1164 (m), 1119 (s), 993 (m), 894 (w), 751 (s), 678 (s), 547 (m), 510 (m).

[Cu(L)SPh] (3). **1** was prepared as before using **L** (0.1002 g, 0.21 mmol) and Cu^I(MeCN)$_4$(BF_4) (0.0675 mg, 0.21 mmol) in CH_2Cl_2 solution (10 mL). NaSPh (0.029 g, 0.22 mmol) was placed in a Schlenk tube under N_2, dry degassed CH_2Cl_2 (5 mL) was added to give a cloudy white suspension. The NaSPh solution was transferred *via* cannula to the solution of **1**. A colour change to intense red was observed over a few minutes. The solution was stirred for 1$\frac{1}{2}$ h and then filtered to removed a fine precipitate. The solvent was reduced to 1 mL and then Et_2O was added to precipitate a fine dark red powder. The powder was collected by filtration, washed with Et_2O (2 × 5 mL) and then dried (0.061 g, 0.09 mmol, 45%). Elemental analysis: $C_{39}H_{38}N_3CuS{\cdot}0.75CH_2Cl_2$ calc C 67.43, H 5.62, N 5.94; found C 67.28, H 5.68, N 6.16%. ^{1}H NMR (CD_2Cl_2): δ 2.00 (d, 1H, $H^{B\prime}$), 2.10 (d, 2H, H^B), 2.36 (d of t, 1H, $H^{A\prime}$), 2.30 (d of t, 2H, H^A), 3.91 (s broad, 1H, tachC*H*, $H^{C\prime}$), 3.96 (s broad, 2H, tachC*H*, H^C), 6.94 (d, 2H, Ph–C*H*=CH–CH=, H^F), 7.01 (d, 1H, Ph–C*H*=CH–CH=, $H^{F\prime}$), 7.23 (m, 8H, ArC*H*, $H^{H\prime}$, $H^{I\prime}$, H^K, H^L, H^J), 7.37 (t, 2H, ArC*H*, H^I), 7.44 (t, 4H, ArC*H*, H^H), 7.73 (d, 1H, ArC*H*, $H^{G\prime}$), 7.76 (d, 2H, ArC*H*, H^G), 7.83 (d of d, 2H, N=CH–C*H*=CH, H^E), 7.98 (d, 1H, N=C*H*–CH, $H^{D\prime}$), 7.99 (d, 2H, N=C*H*–CH, H^D), 8.53 (d of d, 1H, N=CH–C*H*=CH, $H^{E\prime}$). ^{13}C NMR (CD_2Cl_2): 38 (tach-*C*H_2, C1′), 39 (tach-*C*H_2, C1), 65.5 (tach-*C*H, C2′), 66 (tach-*C*H, C2), 126 (*p*-PhS–*C*H, C13), 127 (*ipso*-PhS-*C*, C10), 127 (N=CH–*C*H=CH, 4′), 127.25 (N=CH–*C*H=CH, C4), 127.3 (*o*-PhS–*C*H, C11), 127.5 (*m*-PhS–*C*H, C12). 127.5 (Ar*C*H, C8 and C8′), 128 (Ar*C*H, C7 and C7′), 129 (Ar*C*H, C9 and C9′), 135 (Ar*C*, C6′), 135.5 (Ar*C*, C6), 143 (Ar–*C*H=CH, C5′), 144.5 (Ar–*C*H=CH, C5), 161.5 (N=*C*H–CH C3′), 162.5 (N=*C*H–CH C3). MS (ES): m/z = 534 [^{63}Cu**L**$^+$], 536 [^{65}Cu**L**$^+$], 566 [^{63}Cu**LS**$^+$], 568 [^{65}Cu**LS**$^+$]. IR/cm^{-1} (KBr pressed disk): 3057 (m), 3024 (m), 2911 (m), 2860 (m), 1628 (s, $\nu_{C=N}$), 1294 (w), 1258 (w), 1171 (m), 1128 (m), 1081 (w), 1024 (w), 990 (m), 958 (w), 920 (w), 840 (s), 750 (m), 690 (m), 668 (s), 558 (m).

[Cu(L)NO$_2$] (4). **1** was prepared as before using **L** (0.1002 g, 0.21 mmol) and Cu^I(MeCN)$_4$(BF_4) (0.0658 g, 0.21 mmol) in CH_2Cl_2 solution (10 mL). [NBu_4][NO_2] (0.0633 g, 0.22 mmol) was placed in a separate Schlenk tube and dissolved in CH_2Cl_2 (5 mL) to give a pale yellow solution. This solution was transferred *via* cannula into the solution of **1**. An instantaneous colour change to orange/red was observed. The solution was stirred for $\frac{1}{2}$ h and the volume was then reduced to ~3 mL. The solution was filtered into a pencil schlenk, layered with Et_2O (10 mL) and then left to crystallise. After a few days dark red blocks had formed, they were collected by filtration, washed with Et_2O and then dried (0.0797 g, 0.14 mmol, 66%). Elemental analysis: $C_{33}H_{33}N_4O_2Cu.H_2O$: calc C 66.15, H,5.89, N 9.35; found C 66.33, H 5.70, N 9.17%. Repeated analyses on different batches of **4** gave similar results, indicating the presence of some solvent in the complex. The appearance of a water peak in the NMR spectrum suggests that this solvent is water. Solvent inclusion is not an unusual feature of this type of complex, since the 'cavity' formed by the cinnamyl groups of the ligand traps solvent easily.[23] ^{1}H NMR (CD_2Cl_2): δ 1.5 (s, H_2O), 2.02 (d, 3H, *cis*-tachCH_2, H^B), 2.28 (d of t, 3H, *trans*-tachCH_2, H^A), 3.93 (s broad, 3H, tachC*H*, H^C), 7.07 (d, 3H, Ph–C*H*=CH–CH=, H^F), 7.37 (t, 3H, ArC*H* H^I), 7.45 (t, 6H, ArC*H*, H^H), 7.70 (d, 6H, ArC*H*, H^G), 7.97 (d, 3H, N=C*H*–CH, H^D), 8.06 (d of d, 3H, N=CH–C*H*=CH, H^E). ^{13}C NMR (CD_2Cl_2): δ 38 (tach-*C*H_2, C1), 65.5 (tach-*C*H, C2), 127.5 (N=CH–*C*H=CH, C4), 128 (Ar*C*H, C8), 129 (Ar*C*H, C7), 129.5 (Ar*C*H, C9), 136 (Ar*C*, C6), 144 (Ar–*C*H=CH, C5), 162.5 (N=*C*H–CH C3). MS (ES): m/z = 534 [^{63}Cu**L**$^+$], 536 [^{65}Cu**L**$^+$]. IR/cm^{-1} (KBr pressed disk): 3052 (w), 3019 (w), 2991 (w), 2929 (m), 2909 (m), 2864 (m), 1625 (s, $\nu_{C=N}$), 1585 (m), 1491 (w), 1446 (m), 1417 (w), 1393 (w), 1279 (s), 1168 (m), 1123 (s), 1017 (m), 984 (m), 919 (w), 747 (s), 686 (m), 551 (w), 502 (m).

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