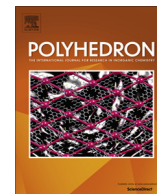




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Synthesis and characterisation of two Cu(I) metalloligands based on tetradentate tripodal ligands

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ABSTRACT

Two new tetradentate tripodal ligands (**L**¹ and **L**²) have been synthesized via Schiff base condensation of tris(2-aminoethyl)amine (tren) with 4-(4-pyridinyl)benzaldehyde or 4-(3-pyridinyl)benzaldehyde in ethanol. Four Cu(I) complexes [CuL¹]PF₆, [CuL¹]I, [CuL²]PF₆ and [CuL²]I (**1–4**) have been prepared and characterised by NMR, HR-MS, SEM-EDS, FT-IR, Raman and UV-Vis measurements. X-ray structures for **1** and **4** are presented. In both structures, the four-coordinate copper(I) centres are bound within the cavity defined by the tren backbone. In such Cu(I) complexes, steric considerations dictate that the three uncoordinated pyridine nitrogen donors will have their coordination vectors oriented in a mutually divergent manner suitable for coordination to three different metal centres and thus are preorganized to act as new tripodal metalloligands.

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1. Introduction

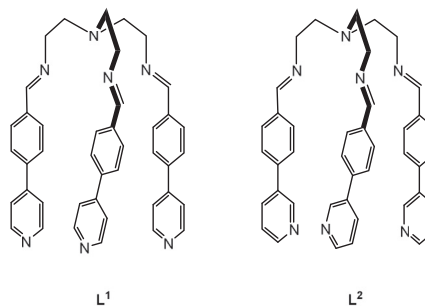
Recently, the design and synthesis of metalloligands for use as building blocks in supramolecular chemistry has been of increasing interest [1–3] due to their usefulness for precisely controlling the construction of larger homo or hetero metallo-supramolecular entities. Despite considerable effort devoted to the development of different metalloligand types, their synthesis for use in producing new supramolecular architectures with designed properties remains a significant challenge [4–10].

Mononuclear tripodal complexes incorporating uncoordinated secondary donor sites consisting of pyridine [4,9,11,12] and imidazole [4,8] nitrogens are typical examples of metalloligands. In these, uncoordinated donor sites at the terminus of each arm of the tripodal complex are available for coordination to a second metal ion.

Tris(2-aminoethyl)amine (tren), incorporating a classic tripodal backbone, is well documented to form complexes with a wide range of transition, post-transition and rare earth metal ions. Condensation of 4-formylimidazole with tren in a 3:1 ratio yields the corresponding “extended” tripodal ligand which, for example, forms 1:1 complexes with Fe(III) or Ln(III) ions, leaving the three imidazole NH groups available (following deprotonation) for coordination to additional metal centres [4,8]. Such an outcome

was recently demonstrated for this system by our group [4,8] using both the Fe(III) and the Dy(III) metalloligands; we were successful in preparing discrete heterometallic Fe(III)/Cu(II) or Dy(III)/Cu(II) polyhedral nanocages. As above, both symmetrical and unsymmetrical metalloligands have been reported by employing metal ions with different coordination number and geometries.

As an extension of our previous studies involving tripodal metalloligands incorporating Fe(III) and Dy(III), we now describe the design and preparation of two new Cu(I) metalloligands using the tetradentate ligands **L**¹ and **L**² (see below). A key feature of our design was to incorporate longer aromatic components that would give rise to larger void cavities as well as providing (potential) additional π - π interactions sites that could aid subsequent host-guest studies.



L¹

L²

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2. Results and discussion

The Schiff base C_3 -symmetric tetradentate ligands **L**¹ and **L**² were prepared in 73% and 76% yield, respectively, from the reaction of tren with 4-(4-formylphenyl)pyridine or 4-(3-pyridinyl)benzaldehyde employing slight modifications of reported procedures [13–15]. ¹H and ¹³C NMR spectra (Figs. S1–4) and high resolution electrospray ionization (HR-ESI) mass spectrometry results were consistent with the proposed structures of **L**¹ and **L**², with the NMR spectra confirming the formation of highly symmetric (C_3) species. In the HR-mass spectra (Figs. S5–6), major peaks for [**L**+H]⁺ were observed at m/z 642.3224 (for **L**¹) and m/z 642.3390 (for **L**²), the appropriate isotope patterns for [**L**+H]⁺ were evident (inserts in Figs. S5–6) with the isotopic distributions in excellent agreement with their simulated patterns. The Cu(I) metalloligands [Cu^I]**L**¹PF₆ (**1**), [Cu^I]**L**¹I (**2**), [Cu^I]**L**²PF₆ (**3**) and [Cu^I]**L**²I (**4**) were obtained as air stable orange solids upon addition of the appropriate copper (I) salt to **L**¹ or **L**² in methanol with the yields ranging from 51 to 66%. ¹H NMR spectra (Figs. S7–10) of complexes **1**–**4** and ¹³C NMR for **1** and **4** (Figs. S11 and S12) were successfully obtained. The proton signals for the aromatic ring and the –CH₂–bridges between N donors in the tren backbone are significantly shifted relative to the respective free ligands.

Single crystals of **1** and **4** were employed for X-ray crystallographic analyses. Complex **1** crystallises in the monoclinic space group $P2_1/c$ with one complex in the asymmetric unit. The Cu(I) centre adopts a distorted tetrahedral geometry with approximate C_3 -symmetry, coordinating to each of the four “tren” nitrogen atoms of the ligand (Fig. 1). The coordination geometry resembles a trigonal bipyramidal arrangement with one of the axial ligands removed such that it approximates a “triangular-based pyramidal” geometry. The Cu–N_{imine} bond lengths are in the range of 2.001(4) Å–2.009(5) Å and the Cu–N_{tertiary} is slightly longer at 2.189(5) Å. The N_{imine}–Cu–N_{imine} angles are close to 120° (118.84(17)–121.23(18)°) and the N_{imine}–Cu–N_{tertiary} angles are in the range 84.88(18)–85.60(17)°. The phenylpyridine groups are involved in intramolecular edge-face π – π stacking between the three adjacent phenyl moieties and the adjacent three pyridyl groups indicated by CH–centroid distances of 3.0–3.5 Å.

Each complex interacts with two adjacent complexes through relatively weak intermolecular offset face-to-face π -stacking between the phenylene and electron-poor pyridine groups (C–centroid separation, 3.6 Å) forming a one-dimensional chain that extends parallel to the crystallographic c -axis (Fig. 2). These chains are arranged into undulating two-dimensional cationic layers in the bc -plane separated by hexafluorophosphate anions which are involved in weak hydrogen bonding (CH...F distances

2.39–2.59 Å) with both aromatic and imine hydrogen atoms acting as donors.

Complex **4** crystallises in the trigonal space group $R\bar{3}$ with one third of the molecule in the asymmetric unit. The molecular and coordination geometry is almost identical to that of **1** with the copper(I) centre again adopting a similarly distorted tetrahedral (“triangular-based pyramidal”) geometry (Fig. 3).

Again, adjacent cations undergo π – π stacking; however, each [Cu^I]**L**² ion interacts with three others forming a honey-comb like

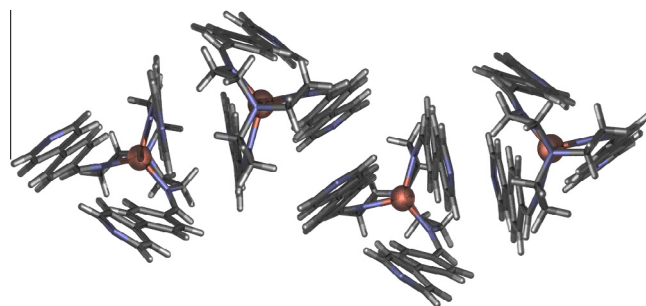


Fig. 2. Schematic representation of part of the packing in the X-ray crystal structure of **1**, illustrating the one-dimensional polymer formed via weak π – π stacking. Anions not shown.

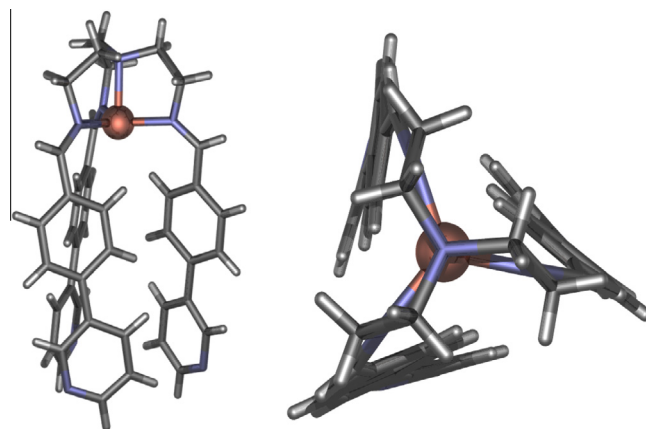


Fig. 3. Schematic representations of the X-ray crystal structure of **4**. The anion is not shown. Selected bonds and angles: Cu – N_{tertiary} 2.167(4) Å, Cu – N_{imine} 2.024(2) Å; N_{imine} – Cu – N_{imine} 119.433(18)°, N_{imine} – Cu – N_{tertiary} 85.66(7)°.

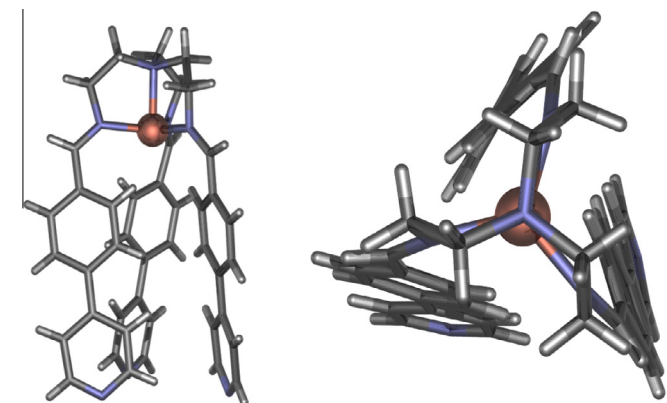


Fig. 1. Schematic representations of the X-ray crystal structure of [Cu^I]**L**¹PF₆. The anion is not shown.

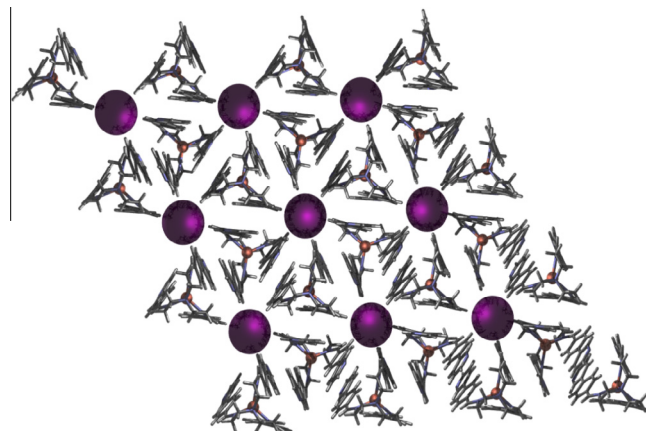


Fig. 4. Schematic representation of part of the packing in the X-ray crystal structure of [Cu^I]**L**²I, illustrating the two-dimensional polymer network formed weak π – π stacking.

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