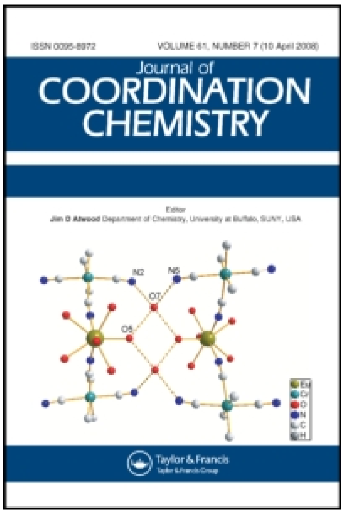

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# Synthesis and crystal structure of a 2nm long rectangular copper dimetallomacrocycle

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# Synthesis and crystal structure of a 2 nm long rectangular copper dimetallomacrocycle[§]

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A new mixed-heterocycle ‘extended-reach’ ligand has been synthesized and used to prepare copper(II) and nickel(II) complexes. An X-ray crystal structure determination reveals that the copper complex is an $M_2L_2$ metallomacrocycle having an unusual rectangular shape with a length of over 2 nm stabilized by intramolecular $\pi$-stacking.

*Keywords*: Copper; N Ligands; Bridging Ligands; Metallomacrocycle

## 1. Introduction

One of the topical areas of supramolecular chemistry is the synthesis of large metallomacrocyclic structures by self-assembly of transition metal ions and appropriately designed organic ligands [1–4]. These metallomacrocycles typically have large voids that make then ideal for construction of catenanes and rotaxanes [2, 5–8] or useful as synthetic receptors and molecular reaction flasks [3, 4, 9].

Fujita and co-workers pioneered much of the initial work in this area with the synthesis and investigations of the dynamic behaviour of dinuclear metallomacrocycles in solution [5–7, 10]. These discrete systems are formed from the self-assembly of divergent polydentate ligands and *cis*-protected transition metal ions [5, 11]. Self-catenation of these systems can be induced by high concentrations and stabilised by edge-to-face $CH \cdots \pi$ interactions [7]. A dimetallomacrocycle containing a fluorinated spacer group has been used to bind electron-rich aromatic guests within the cavity of the metallomacrocycle [3]. In similar rational approaches, other workers have reported the metal-directed self-assembly of dinuclear metallomacrocyclic structures with divergent polydentate ligands based upon, for example, various organic spacers [12, 13], chiral groups [14], fullerenes [15], and metalloporphyrins [16]. These assemblies display interesting host-guest behaviour; for instance ‘Lantern’ complexes based on amide containing ligands bind both anions and cations [13].

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[§]Dedicated to Prof. Peter Williams in honour of his outstanding contribution as editor of this journal

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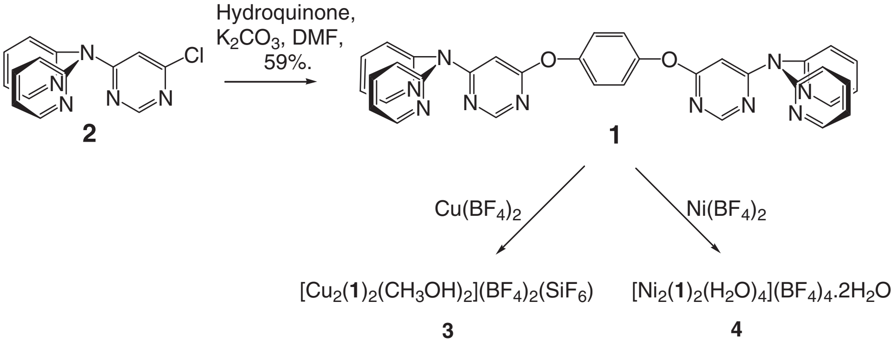
Simple tripodal ligands, which are capable of facial coordination of an octahedral metal atom, represent a very large class of extensively studied compounds in coordination chemistry. These include the $C_3$-symmetric azole and azine containing compounds, for example, tripyrazolylborate [17], tripyrazolylmethane [18] and tri-2-pyridylmethane [19]. Unsymmetrical examples have also been studied [20], as well as ligands incorporating multiple atom tethers between the donor heterocycles [21]. Extension of these simple tripodal motifs to divergent bridging ligands with tripodal binding domains has also been described [19, 22, 23].

We are engaged in study of a class of ligand that consists of a bridging core to which are appended di-2-pyridylmethyl-, or di-2-pyridylamino-substituents [24–26]. These ligands possess two binding domains with a tripodal arrangement of three nitrogen donor atoms. Examples of this ligand class have been studied in various contexts by Lippard and co-workers [27] and Manzur *et al.* [28]. Until recently, we restricted our study of such ditopic tripodal ligands to diazine cores and consequently, to metal-metal separations of up to *ca.* 6.9 Å. One of the main aims of this work was to prepare bridging ligands where the metal-metal distance could be systematically enlarged by altering the core structure of the ligand. As part of our studies of the coordination chemistry of ditopic tripodal ligands we have reacted them with various $M(BF_4)_2$ salts (where M = Co, Ni, Cu, Zn). With these metal precursors we have observed two common structures in the complexes of these tripodal ligands; either side-by-side [2+2] metal-ligand dimers or dinuclear helicates [24]. In this communication we focus on our results for the extended-reach ligand **1** whereby a 2 nm long 38-atom dicopper metallomacrocycle was synthesized (scheme 1) and characterized by X-ray crystallography.

## 2. Experimental

### 2.1. *General Experimental*

Unless otherwise stated reagents were obtained from commercial sources and used as received. The starting material for the synthesis of **1**, 4-chloro-6-(di-2-pyridylamino) pyrimidine (**2**), was prepared as described elsewhere [25]. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected.



Scheme 1. Synthesis of (**1**), (**3**) and (**4**).

The Campbell microanalytical laboratory at the University of Otago performed elemental analyses. Electrospray (ES) mass spectra were recorded using a Micromass LCT-TOF mass spectrometer. NMR spectra were recorded on Varian 300 MHz and Varian 500 MHz spectrometers at 23°C, using a 3 mm probe.

### 2.2. *Preparation of 1,4-bis(6-[di-2-pyridylamino]-4-pyrimidyloxy)benzene (1)*

Compound **2** (250 mg, 0.88 mmol) and 1,4-dihydroxybenzene (48.5 mg, 0.44 mmol) were combined and dissolved in DMF. $K_2CO_3$ (122 mg, 0.87 mmol) was added to this solution and the reaction mixture heated at 120°C for 24 h. The reaction was cooled to room temperature and the DMF removed *in vacuo*. The resulting residue was redissolved in chloroform and filtered through a Celite plug before the filtrate was washed with water, then brine and dried over magnesium sulfate. The solvent was removed *in vacuo* to give a pale brown solid, which was purified by chromatography on alumina (20 g) to give **1** as a cream solid. Yield 314 mg (59%). M.p. 237–239°C. Anal. calcd for $C_{34}H_{24}N_{10}O_2 \cdot ½H_2O$(%): C, 66.55; H, 4.11; N, 22.83. Found: C, 66.66; H, 3.78; N, 22.73. ES-MS: 605.3 $[(M+1)]^+$. $^1H$ NMR ($CDCl_3$) $\delta$ 8.50 (d, 4H, H6″), 8.44 (s, 2H, H2′), 7.75 (t, 4H, H4″), 7.22 (d, 4H, H3″), 7.18 (t, 4H, H5″), 7.16 (s, 4H, H2/H3/H5/H6), 6.49 (s, 2H, H5′). $^{13}C$ NMR ($CDCl_3$) $\delta$ 170.0, 163.9, 158.1, 155.7, 149.7, 138.4, 122.6, 121.4, 121.0, 94.89.

### 2.3. *Preparation of the complexes*

**[$Cu_2(1)_2(CH_3OH)_2](BF_4)_2(SiF_6)$ (3).** $Cu(BF_4)_2$ (11.2 mg, 0.032 mmol) and **1** (20.0 mg 0.033 mmol) were both dissolved in hot methanol and the solutions combined. Immediately a pale blue solid formed. Addition of dichloromethane to the reaction mixture led to the formation of blue crystals of **3** $\cdot$ 8($CH_2Cl_2$) that were suitable for X-ray crystallography. These were collected and dried *in vacuo*. Yield 18.2 mg (66%). M.p. 220–223°C (dec.). Anal. calcd for $C_{70}H_{56}B_2N_{20}O_6F_{14}SiCu_2$(%): C, 48.98; H, 3.30; N, 16.33. Found: C, 48.20; H, 3.28; N, 16.27.

**[$Ni_2(1)_2(H_2O)_4](BF_4)_4 \cdot 2(H_2O)$ (4).** $Ni(BF_4)_2$ (11.2 mg, 0.033 mmol) and **1** (19.9 mg, 0.033 mmol) were both dissolved in hot methanol and the solutions combined. On standing a blue microcrystalline solid precipitated from solution, was collected and then dried *in vacuo*. Yield 8 mg (27%). M.p. >280°C (dec.). Anal. calcd for $C_{68}H_{64}B_4N_{20}O_{10}F_{16}Ni_2$(%): C, 45.72; H, 3.62; N, 15.69. Found: C, 45.68; H, 3.84; N, 15.39.

### 2.4. *X-Ray Crystallography*

The crystal data, data collection and refinement parameters for **3** $\cdot$ 8($CH_2Cl_2$) are given below. The measurements were made with a Siemens CCD area detector using graphite monochromatised Mo K$\alpha$ ($\lambda = 0.71073$ Å) radiation. The intensities were corrected for Lorentz and polarisation effects and for absorption [29]. The structure was solved by direct methods using SHELXS [30], and refined on $F^2$ using all data by full-matrix least-squares procedures using SHELXL-97 [31]. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Hydrogen atoms were included in calculated positions with isotopic displacement parameters 1.2 (aromatic) or 1.5 (aliphatic) times the isotropic equivalent of their carrier carbon atoms.

*Crystal data for* **3**$\cdot$8($CH_2Cl_2$): $C_{78}H_{72}B_2Cl_{16}Cu_2F_{14}N_{20}O_6Si$, *FW* 2395.55, triclinic, *P*-1, *a* 10.757(3), *b* 11.718(3), *c* 21.781(6) Å, $\alpha$ 96.346(4), $\beta$ 95.415(4), $\gamma$ 111.295(4)°, *V* 2515(1) $Å^3$, *Z* 1, $\rho$ 1.581 $Mg/m^3$, $\mu$ 0.945 $mm^{-1}$, *F*(000) 1208, blue plate 0.58 × 0.40 × 0.30 mm, $2\theta_{max}$ 52°, *T* 168 K, 32825 reflections [$R_{int} = 0.0306$], 10124 unique (97.9% completeness), 701 parameters, GOF 1.05, *wR*2 0.187 for all data, *R* 0.060 for 7497 data with $I > 2\sigma(I)$.

## 3. Results and Discussion

A previous synthesis of a related tripodal ligand, 4,6-bis(di-2-pyridylamino)pyrimidine provided a significant amount of monosubstituted compound, 4-chloro-6-(di-2-pyridyl amino)pyrimidine (**2**), as a by-product [25]. It was thought that **2** could be reacted with various substituted benzene cores to form a variety of 'extended-reach' tripodal ligands, analogous to the work of Kodera [22] and Reger [23]. The present 'extended-reach' ligand was prepared by heating **2**, hydroquinone and potassium carbonate overnight in DMF, to give 1,4-bis(6-[di-2-pyridylamino]-4-pyrimidyloxy)benzene (**1**) in 59% yield (scheme 1). While providing large metal-metal separations, a disadvantage with such ligands is that the metal centers of potential dinuclear complexes are no longer connected via a conjugated core, removing the possibility of metal-metal interactions through the $\pi$-system of the ligand. We postulated that this tripodal ligand would be capable of the formation of discrete $M_2L$ complexes or dinuclear metallomacrocycles on reaction with transition metals.

The formation of complexes of **1** was hindered by low solubility of this compound in polar solvents. Reaction with various transition metal precursors invariably led to preferential precipitation of the ligand under the conditions used. This was overcome in certain cases by adding dichloromethane to the reaction mixtures. When copper tetrafluoroborate was reacted with **1**, a blue powder precipitated from the reaction mixture almost immediately. It was induced to crystallize by addition of dichloromethane to the reaction mixture to give **3** in 66% yield. By a combination of elemental analysis and X-ray crystallography, **3** was characterized as $[Cu_2(\mathbf{1})_2(CH_3OH)_2](BF_4)_2(SiF_6)$. Crystals of **3** were obtained as a dichloromethane solvate. A related complex (**4**) was prepared by reaction of **1** with nickel tetrafluoroborate in methanol and isolated as a blue crystalline solid in 27% yield. Elemental analysis on **4** confirmed a 1 : 1 metal-ligand stoichiometry for the complex, and on the basis of the crystal structure of complex **3** and a preference of nickel(II) for octahedral geometries with azine ligands, it is probable that this complex is also a [2+2] dimer with composition $[Ni_2(\mathbf{1})_2(H_2O)_4](BF_4)_4 \cdot 2H_2O$.

The structure of **3** $\cdot$8($CH_2Cl_2$) is a large [2+2] dimetallomacrocycle formed from two molecules of the extended-reach ligand, **1**, and two copper atoms. The use of this ligand leads to a large 38-membered dimetallomacrocyclic ring which has a rectangular shape and a length of 2 nm. The complex crystallizes in the space group *P*-1, with one molecule of **1**, one copper atom, a coordinated methanol molecule, four dichloromethane solvate molecules, one tetrafluoroborate anion and half a hexafluorosilicate anion in the asymmetric unit. The hexafluorosilicate anion is likely to originate from action of hydrofluoric acid (formed from decomposition of the tetrafluoroborate anion in water) on the glass reaction vessel. Three of the dichloromethane solvate molecules are disordered over two sites. A perspective view of the complex is shown in figure 1, with hydrogen atoms and non-coordinated anions and solvate molecules omitted for clarity.

The copper atoms have a distorted square-pyramidal coordination geometry ($\tau$ value of 0.24) with the oxygen atom of the methanol solvate in the apical position (Cu – O = 2.134(3) Å). Despite having eight nitrogen donor atoms available for coordination, only the four pyridine nitrogen atoms of each ligand participate in coordination to copper. All coordinate in the basal positions of the copper(II) centers with bond lengths that range from 2.010(3) to 2.041(3) Å. The pyrimidine donors do not coordinate and thus the ligand is hypodentate in this complex.

The extended-reach ligand **1** has considerable flexibility in its conformation, but in this structure acts as a rigid rod to connect the two copper atoms. Consequently, the Cu-Cu distance is 18.101(1) Å, considerably longer than other [2+2] bimetallic complexes prepared with related ditopic tripodal ligands [24, 28, 32]. This extended structure is stabilised by weak $\pi$-stacking interactions (3.625(6) Å) between the pyrimidine rings of the ligands. Furthermore, the tertiary amines adopt a planar geometry that is observed for other amine bridged ligands [33], which reinforces this rod-like structure, and inhibits coordination by the pyrimidine nitrogen donors. The central arene rings are aligned parallel but significantly offset with no $\pi$-stacking interaction.

In this structure the ligand does not act in the manner originally intended; no coordination by the pyrimidine nitrogen atoms is observed meaning that the tripodal nature of the ligand donor set is not being utilised. Similar behaviour of a tripodal binding domain occurs in selected complexes reported by Reger *et al.*, where not all the donor atoms in a tripodal binding site coordinate to a single metal, or alternatively,

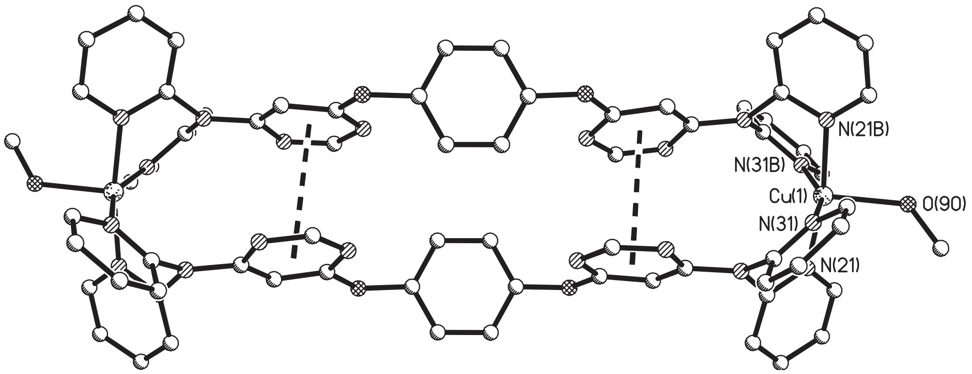


Figure 1. A perspective view of the [2+2]-dimetallomacrocycle **3**, with hydrogen atoms, non-coordinated solvate molecules and anions omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(21) 2.010(3), Cu(1)–N(21′B) 2.029(3), Cu(1)–N(31) 2.032(3), Cu(1)–N(31′B) 2.041(3), Cu(1)–O(90) 2.134(3), N(21)–Cu(1)–N(21′B) 170.64(12), N(21)–Cu(1)–N(31) 87.18(13), N(21′B)–Cu(1)–N(31) 90.75(12), N(21)–Cu(1)–N(31′B) 93.26(13), N(21′B)–Cu(1)–N(31′B) 84.99(12), N(31)–Cu(1)–N(31′B) 156.29(12), N(21)–Cu(1)–O(90) 96.45(12), N(21′B)–Cu(1)–O(90) 92.80(12), N(31)–Cu(1)–O(90) 94.32(12), N(31′B)–Cu(1)–O(90) 109.16(12).

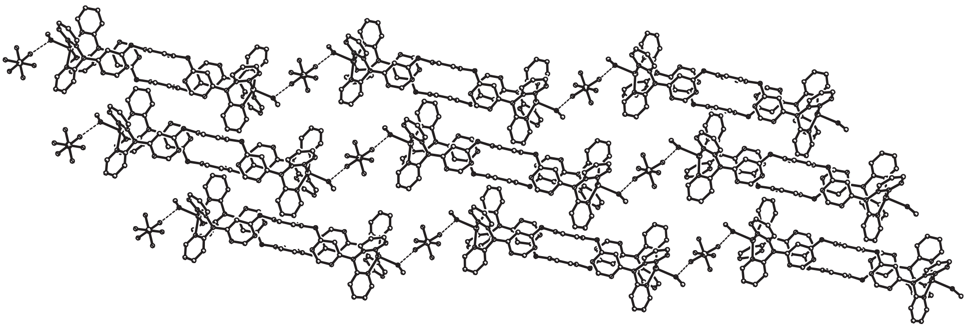


Figure 2. A packing diagram showing the hydrogen-bonded chains of the dimetallomacrocycles.

act as a bridge between two metals [34]. Thus, in this complex, **1** behaves as a bridging doubly bidentate ligand.

A consideration of the packing reveals that the [2+2]-dimers (**3**) are hydrogen bonded into an extended polymeric chain (figure 2). The coordinated methanol molecules hydrogen bond ($d = 1.95(1)$ Å, $D = 2.593(4)$ Å) to an adjacent hexafluorosilicate anion, which acts as a bridge between adjacent molecules of **3**. No other significant interactions affect the packing of the discrete [2+2]-dimers in the crystal.

In summary, we have synthesized an extended-reach ligand that readily forms a large (2 nm long) 38-membered dimetallomacrocyclic ring when reacted with copper(II) tetrafluoroborate. This work paves the way for synthesis and study of structurally related tripodal ligands where control over the bridging geometry and metal-metal distance is possible by altering the aromatic core within the present ligand.

## Supplementary material

Crystallographic data for $3 \cdot 8(CH_2Cl_2)$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC 648879). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

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