

BIS-CHELATION AND ANION EFFECTS INVOLVING A MOLECULE CONSTRUCTED IN THE ORGANIC SOLID STATE USING MOLECULAR TEMPLATES

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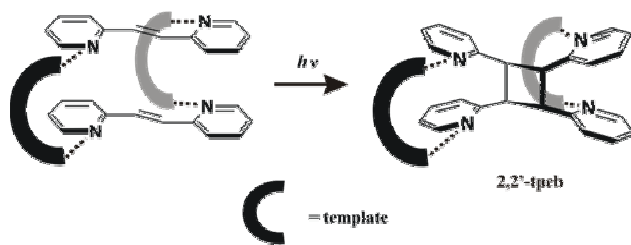
1. ABSTRACT

A molecule derived from a template-directed solid-state synthesis, *rctt*-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb), serves as a bis-chelating ligand upon reaction with $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ and NEt_4PF_6 to produce the dinuclear complex $[\text{Cu}_2(\text{OH})_2(\text{H}_2\text{O})_4(\mu\text{-}2,2'\text{-tpcb})][\text{PF}_6]_2$ (**1**).

2. INTRODUCTION

Transition-metal-ion complexes involving seven-membered chelation rings have emerged as important for applications in catalysis and biology. Specifically, N-C₄-N bridged metallocycles [1] have found applications as catalysts [2] and models of biological compounds [3], as well as antibacterial [4] and antitumor [5] agents. In terms of catalysis, the application of chelating N-donor ligands - as compared to analogous polyphosphines - has begun to attract attention, especially for the activation of C-H bonds [6]. Thus, ligands that provide more than one pyridyl group in close proximity are being studied as preorganized metal chelation units [6b]. In addition, there is increasing interest in the development of novel non-metallocene catalysts for olefin polymerization for which complexes involving N-C₄-N bridged chelate rings have been effective [2c]. Therefore, studies that involve N-C₄-N ligands with a potential to offer seven-membered chelation are of much current interest.

The ability to position molecules in an orientation appropriate for reaction in the organic solid state using molecular templates that operate *via* hydrogen bonds has led to the quantitative and gram-scale construction of molecules difficult to obtain from solution [7,8]. In particular, we have shown that templates based on resorcinol can orient olefins [*e.g.* *trans*-1,2-bis(2-pyridyl)ethylene] (2,2'-bpe)] in the solid state in positions suitable for intermolecular [2+2] photodimerizations. The suitability of the products as ligands for coordination chemistry is evidenced by the presence of pyridine rings that emanate from central cyclobutane rings.



Scheme 1. Template-directed solid-state synthesis of 2,2'-tpcb from 2,2'-bpe.

As part of an ongoing study to elucidate anion effects involving transition-metal-ion complexes of *rctt*-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb), we wish to report here the synthesis and structure determination of the dinuclear Cu(II) complex $[\text{Cu}_2(\text{OH})_2(\text{H}_2\text{O})_4(\mu\text{-}2,2'\text{-tpcb})][\text{PF}_6]_2$ (**1**). In line with our previous study [7], the tetrapyridine acts as a bis-chelating bridge with two Cu(II) centers, giving rise to two seven-membered metallocycles. In contrast to our previous work, the PF_6^- counter ions are non-coordinating and, thus, provide an opportunity for each Cu(II) ion to interact with additional donor units. In the case of **1**, each Cu(II) center is coordinated by two water molecules and a single hydroxide anion, each of which participates in hydrogen bonds with the PF_6^- anion.

3. METHODS

Complex **1** was prepared by combining methanolic solutions of 2,2'-tpcb (0.025 g, 0.068 mmol) [8a] and $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (0.032 g, 0.137 mmol) (1:2 ratio). To the resulting clear blue solution was added a methanolic solution of NEt_4PF_6 (0.037 g, 0.137 mmol) (25 mL methanol total). A 5 mL aliquot of the latter solution was then

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layered with 10 mL benzene in a test tube and allowed to sit for a period of approximately one week. The solution produced blue single crystals (yield: 0.015 g, 29 %) suitable for X-ray analysis [9].

4. RESULTS AND DISCUSSION

Compound **1** crystallizes in the space group $P2_1/n$. An ORTEP perspective of the asymmetric unit of **1** is shown in **Figure 1a**. The asymmetric unit consists of one Cu(II) ion, one-half molecule of 2,2'-tpcb, two water molecules, one hydroxide ion, and one PF_6^- . As shown in **Figure 1b**, the dinuclear complex, which sits around a crystallographic center of inversion, contains one molecule of 2,2'-tpcb that bridges two Cu(II) centers [$d(\text{Cu1}\cdots\text{Cu1a})$ 7.47 Å]. The Cu(II) ions of the complex adopt an *anti* conformation and exhibit a bite angle of 88.8° [10]. Similar to $[\text{Cu}_2(\text{NO}_3)_4(\mu\text{-}2,2'\text{-tpcb})]$ and $[\text{Cu}_2(\mu\text{-SO}_4)_2(\mu\text{-}2,2'\text{-tpcb})(\text{H}_2\text{O})_2]_{\text{PF}_6^-}$, each seven-membered chelation ring adopts a boat conformation. The boat conformation also compares favorably to the chelation complexes of *bis*(2-pyridyl)ethane with Pt(II) [11,12] and 1,2-bis(6-methylpyridin-2-yl)ethane with Pd(II) [13]. The coordination geometry around each Cu(II) center of **1** is square pyramidal. Two pyridyl units of 2,2'-tpcb and two water molecules (O1 and O2) form the base of the pyramid while a hydroxide ion (O3) occupies the apical position. The metal-ligand distances around the base of the pyramid range from 1.96-2.02 Å, while the Jahn-Teller distorted apical distance is 2.21 Å (Table 1).

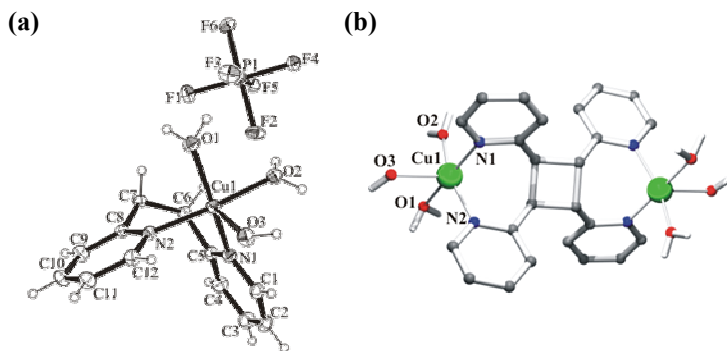


Figure 1. (a) ORTEP representation of the asymmetric unit of **1**. Displacement ellipsoids are drawn at the 30% probability level, with hydrogen atoms being assigned an arbitrary radius; (b) The dinuclear complex **1** (color scheme: green = copper, red = oxygen, blue = nitrogen, grey = carbon). Hydrogen atoms of 2,2'-tpcb have been omitted.

Views of the extended structure of **1** are shown in **Figures 2** and **3**. The complexes have assembled to form layers, parallel to the *ac*-plane, which exhibit an *abab* stacking pattern. The layers are held together by face-to-face π - π forces involving the ligated pyridyl groups (**Figure 2**). The counter PF_6^- ions form layers sandwiched between the layers of Cu(II) complexes. The anions participate in extensive O-H \cdots F hydrogen bonds that involve the two water molecules (O1, O2) and hydroxide ion (O3). Specifically, each PF_6^- anion participates in a total of six O-H \cdots F hydrogen bonds (**Figure 3a**) [$d(\text{O1}\cdots\text{F3})$ 2.750(5) Å; $d(\text{O1}\cdots\text{F4})$ 2.626(5) Å; $d(\text{O2}\cdots\text{F2})$ 2.587(5) Å; $d(\text{O2}\cdots\text{F6})$ 2.600(5) Å; $d(\text{O3}\cdots\text{F1})$ 2.869(5) Å; $d(\text{O3}\cdots\text{F5})$ 2.665(5) Å] (**Figure 3b**) with the ligands.

TABLE 1			
Selected Bond Lengths (Å) and Angles (°) for 1			
Cu1-O1	1.987(4)	O1-Cu1-O2	84.7(2)
Cu1-O2	1.963(4)	O1-Cu1-O3	99.7(2)
Cu1-O3	2.214(4)	O1-Cu1-N2	97.5(1)
Cu1-N1	2.020(4)	O2-Cu1-O3	83.7(2)
Cu1-N2	1.986(4)	O2-Cu1-N1	92.8(2)
		O3-Cu1-N1	101.7(2)
		O3-Cu1-N2	100.5(1)
		N1-Cu1-N2	88.8(1)

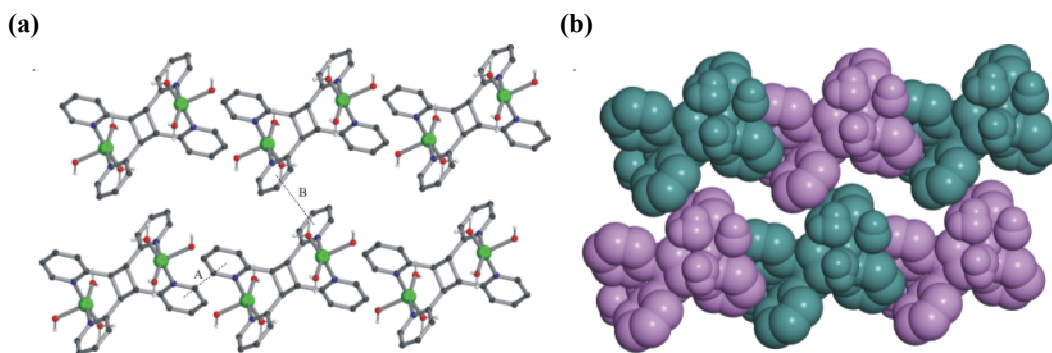


Figure 2. Extended structure of **1** showing the π -stacking of pyridine rings viewed in the ac plane: (a) ball-and-stick representation ($d_A = 3.697(5)$; $d_B = 3.874(5)$ Å) (color scheme: green = copper, red = oxygen, blue = nitrogen, grey = carbon) and (b) space-filling representation (hydrogen atoms of 2,2'-tpcb omitted for clarity).

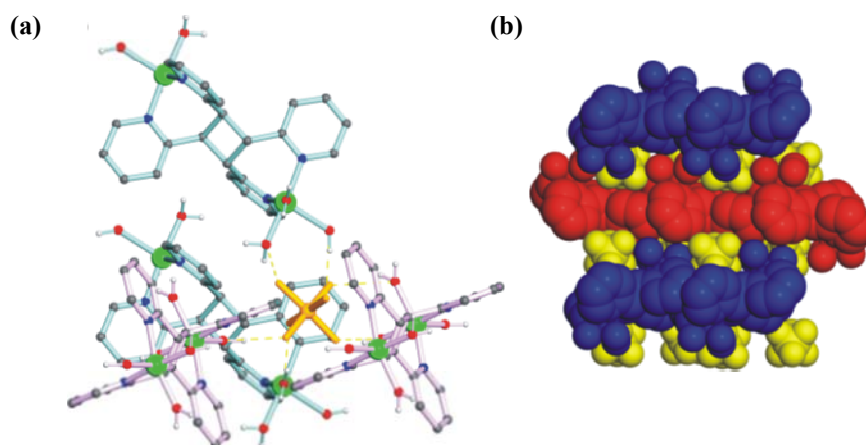


Figure 3. (a) Hydrogen bonding array involving PF_6^- anion (gold) in **1**. Each F-atom is involved in one hydrogen bond (yellow) to a coordinated water or hydroxide molecule of a neighboring assembly (color scheme: green = copper, red = oxygen, blue = nitrogen, grey = carbon, white = hydrogen) (hydrogen atoms of 2,2'-tpcb omitted for clarity) and (b) space-filling representation of **1**, showing $abab$ packing of complex layers alternating with PF_6^- anions. Complexes are shown in red or blue, while PF_6^- anions are shown in yellow.

5. CONCLUSION

In conclusion, template-directed solid-state organic synthesis has led to the construction of a tetrapyrindyl ligand that forms the dinuclear coordination complex **1** with Cu(II) ions. The complex incorporates two seven-membered chelation rings [7]. 2,2'-tpcb is the first ligand to sustain seven-membered chelation in a series of coordination complexes. The non-coordinating behavior of the PF_6^- counter-ion provides open sites on each metal, which are occupied by water molecules and hydroxide ions.

6. REFERENCES

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