

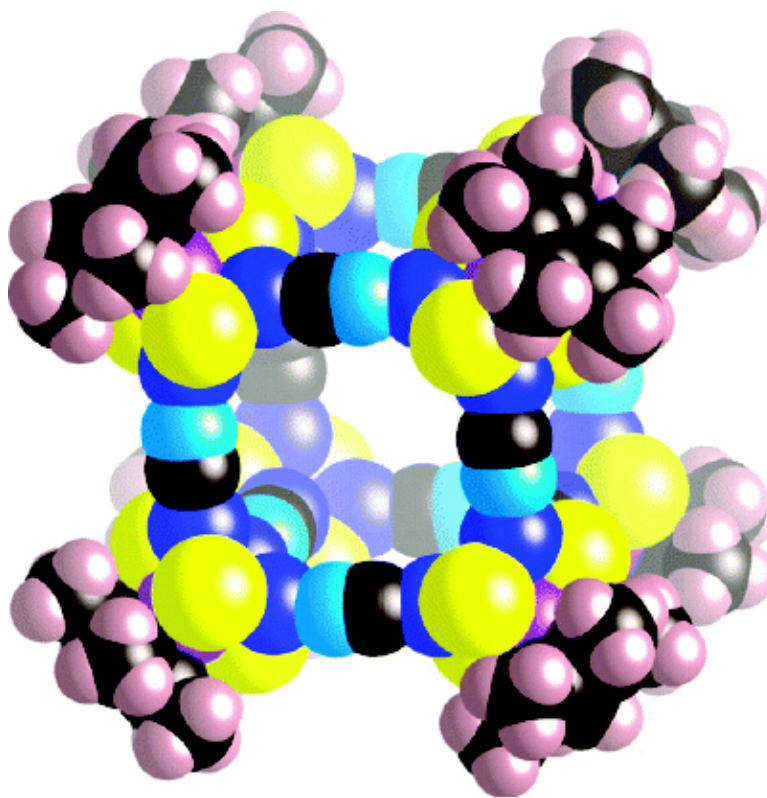
Communication

**Assembly of a Supramolecular Cube, [(Cp\*WSCu)Cl(CN)Li] from a  
Preformed Incomplete Cubane-like Compound [PPh][Cp\*WS(CuCN)]**

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## Assembly of a Supramolecular Cube, $[(\text{Cp}^*\text{WS}_3\text{Cu}_3)_8\text{Cl}_8(\text{CN})_{12}\text{Li}_4]$ from a Preformed Incomplete Cubane-like Compound $[\text{PPh}_4][\text{Cp}^*\text{WS}_3(\text{CuCN})_3]$

Jian-Ping Lang,<sup>\*,†,§</sup> Qing-Feng Xu,<sup>†</sup> Zhong-Ning Chen,<sup>§</sup> and Brendan F. Abrahams<sup>\*,‡</sup>

School of Chemistry and Chemical Engineering, Suzhou University, 1 Shizi Street, Suzhou 215006, Jiangsu, China, State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian, China, and School of Chemistry, University of Melbourne, Victoria 3010, Australia

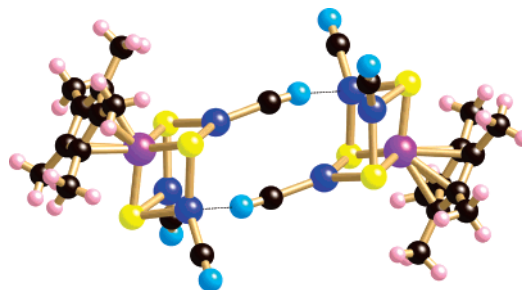
Received July 1, 2003; E-mail: jplang@suda.edu.cn; bfa@unimelb.edu.au

In the past decade, considerable effort has been directed toward developing a rational approach to the generation of supramolecular squares, rings, knots, and boxes. Such species are not only aesthetically appealing but are also of interest because of potential applications in areas such as molecular recognition, catalysis, and optoelectronics.<sup>1–6</sup> The synthesis of molecular cubes has been the focus of particular attention, perhaps because the cube is the most common platonic solid encountered in the macroworld. Despite the interest in cubes, only a few examples of supramolecular cubes have been reported,<sup>7–9</sup> and their generation represents a significant challenge.

Stang has proposed a general design approach for the generation of supramolecular species that are structurally related to common geometrical shapes. In the case of the cube, the strategy proposed is to bring eight tritopic units with 90° angles together with 12 linear ditopic linkers. In  $[\{\text{Ru}(\text{[9]ane-S}_3)\}_8(\mu\text{-}4,4'\text{-bipy})_{12}]^{16+}$  the  $\{\text{Ru}(\text{[9]ane-S}_3)\}$  unit serves as the tritopic corners of the cube, while the 4,4'-bipy ligand is the ditopic linker. In other examples of cubes, cyanides have been shown to be effective ditopic linkers. The cubic complex  $\{\text{M}[\text{Cp}^*\text{Rh}(\text{CN})_3]_4[\text{Mo}(\text{CO})_3]_4\}^{2-}$  ( $\text{M} = \text{K}^+, \text{Cs}^+$ ) was isolated from reactions of  $[\text{Cp}^*\text{Rh}(\text{CN})_3]^-$  with equimolar  $[(\eta^6\text{-C}_6\text{H}_5)\text{Mo}(\text{CO})_3]$  in the presence of  $\text{K}^+$  or  $\text{Cs}^+$ ,<sup>8</sup> while reactions of  $[(\text{tacn})\text{M}'(\text{CN})_3]^{3-}$  with  $[(\text{tacn})\text{M}(\text{H}_2\text{O})_3]^{3+}$  gave rise to several Prussian blue analogues (e.g.,  $[(\text{tacn})_8\text{M}_4\text{M}'_4(\text{CN})_{12}]^{12+}$ ,  $\text{M} = \text{Cr}, \text{Co}$ ;  $\text{M}' = \text{Co}$ ).<sup>9a,d</sup>

For some time now we have been interested in employing preformed  $\text{W}(\text{Mo})\text{-S-Cu}$  clusters as multi-connecting units in supramolecular species.<sup>10</sup> For example, the treatment of  $[(\text{Cp}^*\text{WS}_3)_3\text{-Cu}_7(\text{MeCN})_9](\text{PF}_6)_4$  with pyrazine (pz) in the presence of LiCl yielded a two-dimensional sheet structure of formula  $[\text{Cp}^*\text{WS}_3\text{-Cu}_5\text{Cl}(\text{MeCN})(\text{pz})]_\infty(\text{PF}_6)_\infty$ .<sup>10a</sup> Our general interest in such clusters prompted an investigation of whether  $\text{W}(\text{Mo})\text{-S-Cu}$  units were capable of acting as tritopic corners in a supramolecular cube.

The reaction of  $[\text{PPh}_4][\text{Cp}^*\text{WS}_3]^{11}$  with 3 equiv of  $\text{CuCN}$  in MeCN yields the compound  $[\text{PPh}_4][\text{Cp}^*\text{WS}_3(\text{CuCN})_3]$  (**1**) in 75% yield.<sup>12</sup> As shown in Figure 1, the anion  $[\text{Cp}^*\text{WS}_3(\text{CuCN})_3]^-$  consists of a  $\text{Cp}^*$  ligand bound to the W center of an incomplete  $\text{WS}_3\text{Cu}_3$  cubane-like core with a cyanide group coordinated to each Cu center through the carbon atom.<sup>13</sup> Each Cu atom has an approximate trigonal planar geometry with two  $\mu_3\text{-S}$  atoms and a carbon atom from the terminal cyanide. The  $\text{WS}_3\text{Cu}_3$  core is similar to those found in  $[\text{PPh}_4]_2[\text{Cp}^*\text{WS}_3(\text{CuX})_3]_2$  ( $\text{X} = \text{Br}, \text{Cl}, \text{SCN}$ ).<sup>14</sup> The arrangement of atoms within the cluster results in the three cyanides extending in directions that are approximately perpendicular to each other. The geometry of this unit would appear to



**Figure 1.** Pair of centrosymmetrically related  $[\text{Cp}^*\text{WS}_3(\text{CuCN})_3]^-$  anions. The dotted line represents a  $\text{Cu}\cdots\text{N}$  contact of 2.44 Å. W, Cu, S, N, C, and H atoms are represented by purple, blue, yellow, light blue, black, and pink spheres, respectively.

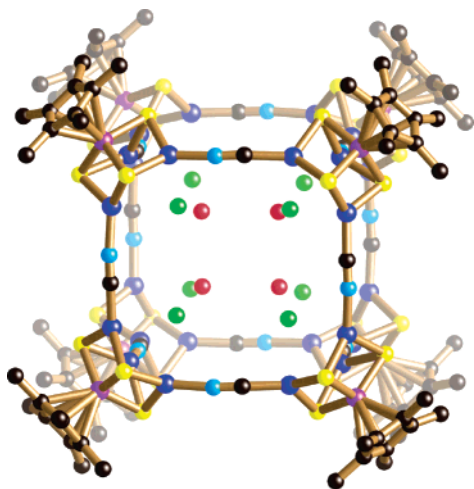
make it an attractive candidate for the role of a three-connecting node in a supramolecular cube. One cyanide unit from each cluster forms a weak coordinate interaction through the nitrogen atom to a Cu atom from another cluster ( $\text{Cu-N}$  2.44 Å). Pairs of these weak interactions result in the formation of centrosymmetrically related dimers as indicated in Figure 1.

Following the successful generation of **1**, we combined it with pyrazine and LiCl in the hope that the bridging ligands would link the clusters to form a cube comprising twelve pyrazines and eight three-connecting  $\text{Cp}^*\text{WS}_3\text{CuCl}$  clusters. The product isolated from this reaction was a cube-related structure but not the one expected. Instead of pyrazine bridges between clusters, cyanide anions link the  $\text{Cp}^*\text{WS}_3\text{Cu}_3$  clusters to form a supramolecular cube of formula  $[(\text{Cp}^*\text{WS}_3\text{Cu}_3)_8(\text{CN})_{12}\text{Cl}_8\text{Li}_4]$  (**2**) (Figure 2). The crystals isolated have the formula  $\mathbf{2}\cdot 2\text{LiCN}\cdot\text{solvate}$ .<sup>15</sup> The crystals readily lose solvent upon exposure to air which results in the loss of single-crystal character. The desolvated compound is air-stable and insoluble in solvents such as MeCN, DMSO, and DMF.

The framework of the cube has the formula:  $[(\text{Cp}^*\text{WS}_3\text{Cu}_3)_8(\text{CN})_{12}]^{4+}$ . All  $\text{Cp}^*\text{WS}_3\text{Cu}_3$  clusters are symmetry related, but there are two types of cyanide links; one type oriented parallel with the unique axis and the other perpendicular to this axis.<sup>16</sup> Both types display C/N disorder, and as a consequence the clusters within the cube cannot all be coordinated by the same donor atom set despite the fact that they are related by crystal symmetry. Although the structure possesses the topology of the cube, the molecule is, in fact, tetragonally distorted. The “cube” dimensions as judged by the separation of W centers are 9.64 Å  $\times$  10.10 Å  $\times$  10.10 Å.

Inside each cube are eight  $\text{Cl}^-$  ions. Each of the chloride ions is associated with a cluster and shows significant positional disorder. In the refinement, the chloride ions were modeled over three sites that are in close proximity to each other. Although the average charge associated with each corner of the cube is +1/2 (obtained by dividing the 4+ charge on the  $[(\text{Cp}^*\text{WS}_3\text{Cu}_3)_8(\text{CN})_{12}]^{4+}$  unit

<sup>†</sup> Suzhou University.  
<sup>§</sup> Chinese Academy of Sciences.  
<sup>‡</sup> University of Melbourne.



**Figure 2.**  $[(\text{Cp}^*\text{WS}_3\text{Cu}_3)_8(\text{CN})_{12}]^{4+}$  “cube” with the eight  $\text{Cl}^-$  and four  $\text{Li}^+$  ions included, viewed along a direction almost parallel to the tetragonal axis. The C/N assignment of the cyanide units in this representation is arbitrary. Only one of the three crystallographically unique sites for the chloride is represented (the site shown was refined with 60% occupancy). W, Cu, Cl, S, N, C, and Li atoms are represented by purple, blue, green, yellow, light blue, black, and red spheres, respectively. H atoms have been omitted for clarity. The assignment of the lithium ions is only tentative.

by 8), the disorder of the polar cyanide anion means that there is likely to be a disparity in the net charge at each corner. Under these circumstances it is not surprising to find some variation in the extent of the chloride-cluster interactions within the cube. With the eight  $\text{Cl}^-$  ions located in the corners, the cube has a net  $-4$  charge. It is difficult to unambiguously identify lithium ions in a crystal structure particularly in a unit cell that contains 16 W and 48 Cu atoms; nevertheless, four symmetry-related peaks were identified at the heart of the cube, and these have been tentatively assigned as lithium ions.

Preliminary photochemical and photophysical investigations of **1** and **2** reveal very interesting photoluminescent properties in the solid state at ambient temperature (see Supporting Information). Excitation of **1** at 435 nm resulted in a broad emission band at 600 nm, while that of **2** at 550 nm gave a relatively narrow emission with  $\lambda_{\text{max}}$  located at 710 nm. There is a remarkable red-shift (more than 100 nm) between the excitations or emissions of **1** and **2**. Such a marked difference may result from the difference in charge and donor atoms found for the  $[\text{Cp}^*\text{WS}_3\text{Cu}_3]$  cluster in **1** and **2**.

In summary, the present work represents an example where the assembly of a novel large supramolecular cube has been achieved through a combination of serendipity and the employment of geometric principles. Investigations of this system are continuing in an effort to determine if multicharged cations could occupy the intracube void and, if so, to examine the effect on the luminescent properties. In this regard lanthanide(III) ions may be useful cations that may be expected to yield an overall uninegative cube.

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**Supporting Information Available:** Crystallographic data for **1** and **2**: $2\text{LiCN}\cdot\text{solvate}$  (CIF); further synthetic details and excitation and emission spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) To a red solution of  $[\text{PPh}_4][\text{Cp}^*\text{WS}_3]$  (100 mg, 0.13 mmol) in MeCN (10 mL) was added CuCN (46 mg, 0.52 mmol). The solution quickly turned dark red, and the mixture was stirred at room temperature for 5 h and then filtered. Diethyl ether (20 mL) was carefully diffused into the filtrate to form red prisms of **1**, which were isolated by filtration, washed with  $\text{Et}_2\text{O}$ , and dried in vacuo. Yield: 70 mg (75%). Anal. Calcd. For  $\text{C}_{37}\text{H}_{35}\text{Cu}_3\text{N}_3\text{PS}_3\text{W}$ : C, 43.85; H, 3.45; N, 4.11. Found: C, 43.78; H, 3.42; N, 4.14. IR (KBr pellet):  $\nu$  (CN) 2129 (m),  $\nu$  (W-S<sub>br</sub>) 428 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (ppm, DMSO- $d_6$ ):  $\delta$  7.16–7.99 (20H, m,  $\text{PPh}_4^+$ ), 2.05 (15H, s,  $\text{Cp}^*$ ).
- (13) Crystal data for **1**:  $\text{C}_{37}\text{H}_{35}\text{Cu}_3\text{N}_3\text{PS}_3\text{W}$ ,  $M = 1023.35$ , triclinic, space group  $P-1$ ,  $a = 9.716(7)$  Å,  $b = 13.917(9)$  Å,  $c = 14.745(10)$  Å,  $\alpha = 101.404(11)^\circ$ ,  $\beta = 98.752(11)^\circ$ ,  $\gamma = 91.087(9)^\circ$ ,  $V = 1929.2(23)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.762$  g/cm<sup>3</sup>,  $\mu$  (Mo K $\alpha$ ) = 48.40  $\text{cm}^{-1}$ ,  $T = 193$  K,  $R = 0.060$ ,  $R_w = 0.064$ , GOF = 1.069.
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- (15) A 3 mL MeCN solution of **1** (51.5 mg, 0.05 mmol) was placed at the end of a zigzag glass tube followed by 4 mL of MeCN that served as a buffer band. A 5 mL MeOH solution of pyrazine (8 mg, 0.1 mmol) and LiCl (1.0 mg, 0.25 mmol) was slowly added followed by 10 mL of  $\text{Et}_2\text{O}$  which was carefully layered onto the methanol solution. Red crystalline prisms of  $2\cdot\text{LiCN}\cdot\text{solvate}$  formed after 3–4 days, and these were separated from some yellowish-red solids. The red prisms were washed with MeCN and  $\text{Et}_2\text{O}$  and dried in vacuo. Yield for  $2\cdot\text{LiCN}$ : 6.78 mg (19.6%). Anal. Calcd for  $\text{C}_{94}\text{H}_{120}\text{Cl}_8\text{Cu}_{24}\text{Li}_6\text{N}_{14}\text{S}_{24}\text{W}_8$ : C, 20.39; H, 2.19; N, 3.54; Cl, 5.12; Li, 0.75; W, 26.56; Cu, 27.55. Found: C, 20.48; H, 2.26; N, 3.46; Cl, 5.20; Li, 0.70; W, 26.20; Cu, 27.31. IR (KBr pellet):  $\nu$  (CN) 2160 (s),  $\nu$  (W-S<sub>br</sub>) 412 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO, 25 °C):  $\delta$  2.060 (15 H, s,  $\text{C}_5\text{Me}_5$ ) ppm.
- (16) Crystal data for  $2\cdot\text{LiCN}\cdot 4.5(\text{C}_2\text{H}_5)_2\text{O}\cdot 4\text{CH}_3\text{CN}\cdot 4\text{CH}_3\text{OH}$ :  $\text{C}_{124}\text{H}_{1193}\text{Cl}_8\text{Cu}_{24}\text{Li}_6\text{N}_{18}\text{O}_{8.5}\text{S}_{24}\text{W}_8$ ,  $M = 6162.62$ , tetragonal, space group  $I4/m$ ,  $a = 17.131(3)$  Å,  $c = 33.136(9)$  Å,  $V = 9723.8(36)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 2.105$  g/cm<sup>3</sup>,  $\mu$  (Mo K $\alpha$ ) = 76.88  $\text{cm}^{-1}$ ,  $T = 193$  K,  $R = 0.063$ ,  $R_w = 0.072$ , GOF = 1.197.

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