

Self-assembly of the cyclic dimer $[\text{Cu}(\text{hfac})_2(\text{bpmu})]_2$ ($\text{bpmu} = N,N'$ -bis(3-pyridylmethyl)urea; $\text{hfac} = \text{hexafluoroacetylacetonate ion}$) using coordination chemistry and predictable $\text{O}=\text{C}(\text{N}-\text{H})_2 \cdots \text{O}=\text{C}$ hydrogen bonds

Juan Granifo ^{a,*}, María T. Garland ^b, Ricardo Baggio ^c

^a *Departamento de Ciencias Químicas, Facultad de Ingeniería, Ciencias y Administración, Universidad de La Frontera, Casilla 54-D, Temuco, Chile*

^b *Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile and CIMAT, Avda. Blanco Encalada 2008, Casilla 487-3, Santiago, Chile*

^c *Departamento de Física, Comisión Nacional de Energía Atómica, Av. Gral Paz 1499, 1650 San Martín, Pcia. de Buenos Aires, Argentina*

Abstract

A novel binuclear metallacyclic complex, $[\text{Cu}(\text{hfac})_2(\text{bpmu})]_2$, was isolated by reacting copper(II) hexafluoroacetylacetonate with the bpmu ligand. The crystal structure reveals the presence of dimetal units with the $\text{Cu}(\text{II})$ centers in a six-coordinate environment and bridged by the bpmu spacers. The crystal consists of a racemate with the two copper(II) ions of one dimer molecule carrying either a $\Delta\Delta$ or $\Lambda\Lambda$ configuration. The pyridyl-urea-based spacers are connected intramolecularly by the expected strong urea-based hydrogen bonds $\text{O}=\text{C}(\text{N}-\text{H})_2 \cdots \text{O}=\text{C}$. The same type of H-bonds allows the molecular units of the same chirality to assemble forming supramolecular columns. This conformationally defined array and hydrogen-bonding network, together with the bulky properties of the fragment $\{\text{Cu}(\text{hfac})_2\}$, were used as a pre-programmed supramolecular information for controlling the formation of discrete species.

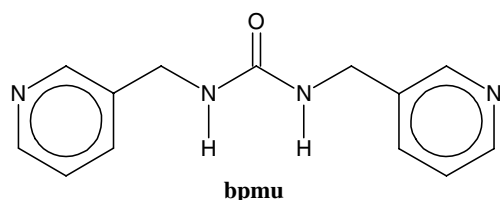
Keywords: Dimeric copper(II) complexes; Polypyridine complexes; N,N' -bis(3-pyridylmethyl)urea; Supramolecular chemistry; Hydrogen bonded assembly

Among the rational strategies for supramolecular synthesis, the host-guest approach has been considered a very powerful tactic for controlling, for example, the self-assembly of structures involving pyridyl-substituted ureas such as N,N' -bis(3-pyridylmethyl)urea (bpmu ; [Scheme 1](#)) [1,2]. Essentially, this approach takes into account the self-assembly capacity of the bipyridine compound by using its predictable $\text{O}=\text{C}(\text{N}-\text{H})_2 \cdots \text{O}=\text{C}$ synthons [3] to generate networks with a typical repeat

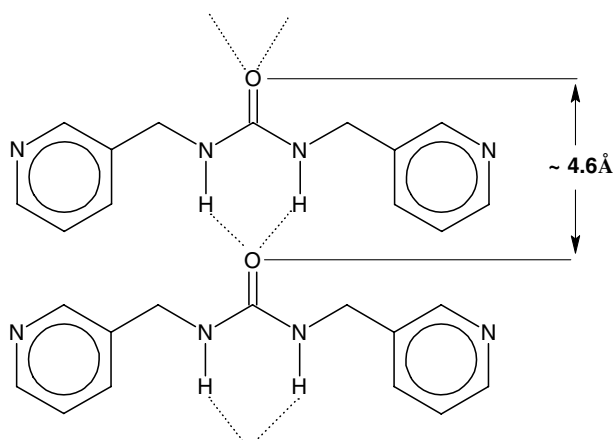
distance of ca. 4.60 Å ([Scheme 2](#)). Then, this preformed net can be imposed to guest molecules, such as dicarboxylic acids, which act as H-bond donors towards the N -pyridyl atoms of the derivatized-urea host [1,2]. In this context, the rationally designed pyridyl-urea bpmu was then envisioned as a “ligand host”, which could control the spacing of metal atoms according to the size of the hydrogen-bonding synthons. The hypothesized result was validated through the reaction of bpmu with the silver salt AgBF_4 , which gave the 1:2 metal-to-ligand coordination polymer $[\text{Ag}(\text{bpmu})_2]\text{BF}_4$ [1]. The X-ray structure consisted of infinite 2D layers joined by the anticipated $\text{O}=\text{C}(\text{N}-\text{H})_2 \cdots \text{O}=\text{C}$ synthons with spacings of 4.625 Å.

* Corresponding author. Tel.: +00 56 45325434; fax: +00 56 45325440.

E-mail address: jgranifo@ufro.cl (J. Granifo).



Scheme 1.



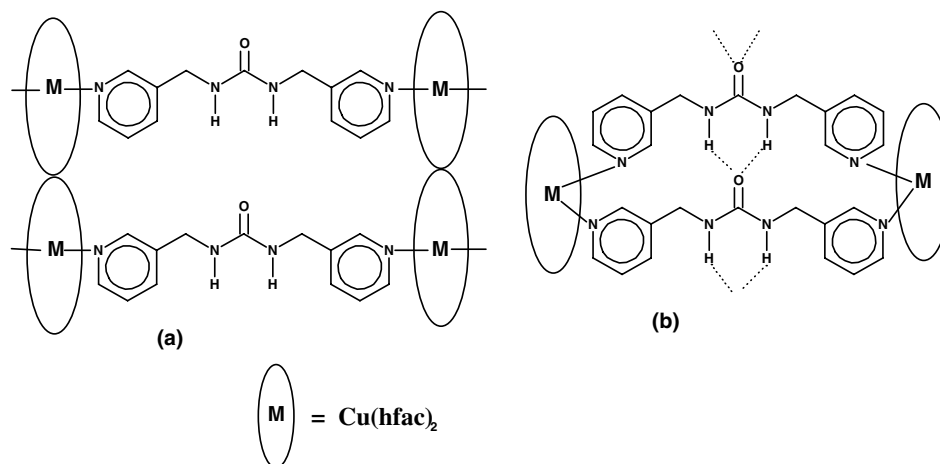
Scheme 2.

On each layer the pyridyl nitrogen atoms of the bifunctional ligands appear coordinated to flattened tetrahedral silver(I) centers to give a net of tetranuclear cycles. A similar interaction has been observed recently in the 1:2 coordination polymer $[\text{Cu}(\text{bpmu})_2(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{EtOH}$, where the bifurcated $\text{O}=\text{C}(\text{N}-\text{H})_2 \cdots \text{O}=\text{C}$ hydrogen bonds appear as intralayer connectors (4.626 Å) [4].

The formation of discrete metallomacrocycles or coordination polymers in transition metal complexes depends primarily on the coordination preferences of the metal centers, the metal to ligand ratio, the characteristics of the organic ligand (e.g., length, flexibility and shape), the donor properties of the counter-ions (coordinated or uncoordinated) and the reaction conditions [5]. Then, a careful handling of these aspects can conduce to an important degree of predictability and control over the structural motifs of the products. Considering these facts and that only 1:2 metal-to-ligand complexes with the bpmu ligand are known [1,4], we have decided to investigate about the architecture that would have a 1:1 metal–bpmu complex prepared under the condition that the organic tecton participates with its normal directional forces (hydrogen-bonding synthons and coordination bonds), i.e., playing the role of a “ligand host”. The accomplishment of these objectives implies to choose a coordination metal system that allows to form specifically complexes with bis(pyridyl) bridging ligands (L) in a 1:1 molar ratio, including escort counter-ions that do not interfere with the design of the H-bonding network controlled by the bpmu ligand. An appropriate

type of compounds are the metal(II) complexes $[\text{M}(\text{hfac})_2]$ ($\text{M} = \text{Mn}, \text{Co}, \text{Cu}, \text{Zn}$; hfac = hexafluoroacetylacetonate), which show a high affinity towards rigid or flexible N,N' -bidentate spacers, producing either coordination polymers or discrete molecular species with a 1:1 metal-to-ligand ratio [6–22]. In this reaction, the $[\text{M}(\text{hfac})_2]$ complexes serve as the source of the coordinatively unsaturated fragments $\{\text{M}(\text{hfac})_2\}$. More specifically, the coordination polymers are formulated as the *cis*- or *trans*- $[\text{M}(\text{hfac})_2(\text{L})]$ species in which the cations are octahedrally coordinated by four oxygen atoms of the chelating hfac units, and two nitrogen atoms from two different linkers [6–22]. On the other hand, the known discrete molecular compounds are only the solvated binuclear metallacycles *cis*- $[\text{Mn}(\text{hfac})_2(\text{bpy})]_2 \cdot n\text{S}$ (bpy = 1,3-bis(4-pyridyl)propane; $n = 1, 2$; S = organic solvent) [21,22]. The assembly of the bpy-based dimeric species is dependent on the reaction conditions and concretely of the solvents used in the crystallization process. The specific solvent that cocrystallizes with a macrocyclic metal complex acts as a template in the creation of the (2,2) cyclic system. On contrary, in absence of the template solvent the product is the helical coordination polymer *cis*- $[\text{Mn}(\text{hfac})_2(\text{bpy})]$ [21]. Indeed, without some special condition, like template solvents, the formation of discrete species involving divergent ligands such as 4,4'-bipyridine is not expected; the structure of a resultant product with 1:1 M–L ratio should consist only of polymeric chains [5]. In this report, we inform about the effect of the conformationally predesigned H-bonding of the bpmu ligand in the formation of the new dimeric metallacyclic complex *cis*- $[\text{Cu}(\text{hfac})_2(\text{bpmu})]_2$. Discrete structures can be reasonably anticipated as a possibility of admitting an ideal behavior as “ligand host” of the bpmu ligand when interacting with the *cis* orientated $\{\text{Cu}(\text{hfac})_2\}$ fragments. A *trans* orientation implies the formation of a 1D coordination polymer with the bulky $\{\text{Cu}(\text{hfac})_2\}$ fragments coordinating to *N*-pyridyl atoms, but this precludes the bpmu ligands to be close enough as to form the expected H bonds of the $\text{O}=\text{C}(\text{N}-\text{H})_2 \cdots \text{O}=\text{C}$ synthons (Scheme 3). Contrarily, the *cis* configuration allows the guest fragments to connect two contiguous ligands belonging to the same or different stacked networks to produce some type of cyclic system (Scheme 3).

The $[\text{Cu}(\text{hfac})_2(\text{bpmu})]_2$ complex was isolated from a methanol solution by treatment of $\text{Cu}(\text{hfac})_2 \cdot \text{H}_2\text{O}$ with the bpmu ligand [23]. Single X-ray crystal analysis [24] reveals that the structure consists of dimeric units formulated as $[\text{Cu}(\text{hfac})_2(\text{bpmu})]_2$ (Fig. 1) and constitutes the first non-polymeric bpmu complex reported. The single bpmu moiety per monomer is actually achieved by the presence of two independent hemi-molecules (labeled C and D) each one bisected by a twofold axis through the urea C=O bonds. The resulting pair of complete bpmu units displays very similar cores; a L.S.



Scheme 3. Schematic representation of the bulky effect of the {Cu(hfac)₂} fragment when interacting with the “ligand host” bpmu ligand. Two possible structures are shown with the metal center in *trans* configuration (a) and *cis* configuration (b).

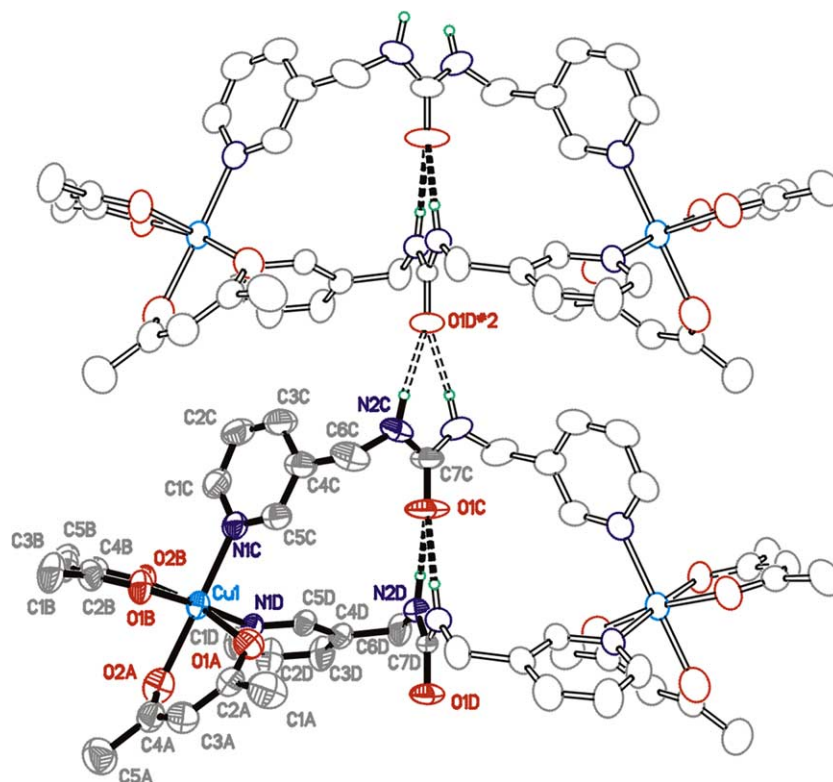


Fig. 1. View of the dimeric units of the [Cu(hfac)₂(bpmu)]₂ complex (only independent part represented in bold lining). In heavy broken lines, intradimeric N–H···O bonds; in double broken, inter-dimeric ones. Displacement ellipsoid drawn at a 40% probability level. Terminal fluorine atoms attached to C1A, C5A, C1B, C5B and hydrogens attached to carbon, not represented for the sake of clarity. Selected bond lengths (Å) and angles (°): Cu(1)–O(1B) 1.965(3), Cu(1)–N(1D) 2.006(3), Cu(1)–O(2B) 2.137(3), Cu(1)–N(1C) 2.143(3), Cu(1)–O(1A) 2.149(3), Cu(1)–O(2A) 2.171(3), C(1A)–C(2A) 1.513(6), C(2A)–C(3A) 1.389(6), C(3A)–C(4A) 1.384(6), C(4A)–C(5A) 1.510(7), O(1B)–C(2B) 1.241(4), O(2B)–C(4B) 1.246(4); C(1B)–C(2B) 1.546(6), C(2B)–C(3B) 1.381(6), C(3B)–C(4B) 1.389(5), C(4B)–C(5B) 1.547(6), N(1C)–C(1C) 1.325(5), N(1C)–C(5C) 1.336(5), N(2C)–C(7C) 1.332(5), N(2C)–C(6C) 1.444(7), O(1C)–C(7C) 1.232(7), C(1C)–C(2C) 1.371(7), C(2C)–C(3C) 1.368(7), C(3C)–C(4C) 1.373(6), C(4C)–C(5C) 1.384(6), C(4C)–C(6C) 1.496(7), C(7C)–N(2C)# 1.332(5), N(1D)–C(1D) 1.318(5), N(1D)–C(5D) 1.331(4), N(2D)–C(7D) 1.329(4), N(2D)–C(6D) 1.435(5), O(1D)–C(7D) 1.227(6), C(1D)–C(2D) 1.356(6), C(2D)–C(3D) 1.368(6), C(3D)–C(4D) 1.371(6), C(4D)–C(5D) 1.364(5), C(4D)–C(6D) 1.512(5), C(7D)–N(2D)# 1.329(4) and O(1B)–Cu(1)–N(1D) 176.92(12), O(1B)–Cu(1)–O(2B) 88.88(11), N(1D)–Cu(1)–O(2B) 91.03(11), O(1B)–Cu(1)–N(1C) 88.91(12), N(1D)–Cu(1)–N(1C) 94.15(12), O(2B)–Cu(1)–N(1C) 96.81(13), O(1B)–Cu(1)–O(1A) 89.77(12), N(1D)–Cu(1)–O(1A) 89.82(12), O(2B)–Cu(1)–O(1A) 170.46(11), N(1C)–Cu(1)–O(1A) 92.60(12), O(1B)–Cu(1)–O(2A) 85.08(12), N(1D)–Cu(1)–O(2A) 91.84(12), O(2B)–Cu(1)–O(2A) 87.57(11), N(1C)–Cu(1)–O(2A) 172.51(12), O(1A)–Cu(1)–O(2A) 82.91(11) (Symmetry transformations used to generate equivalent atoms: # –x,y,–z + 1/2).

fit performed with XP in SHELXTL/PC gave a mean atomic deviation of 0.10 Å for atoms O1, C7, N2, C6, C4 and their symmetry related ones. The main difference between the molecules resides in the rotation of the pyridyl rings around the methyl bond (ca. 50°). The extended bpmu ligands act as bridges between the symmetry related metallic centers, providing two bonds to each coordination octahedron. The remaining four come from two chelating hfac anions (units A and B) at each side. Three of the four CF₃ groups show a clear rotational disorder and have been refined with a split model. Both hfac anions coordinate in a different way, unit A with the molecular and coordination planes being almost parallel (slanting angle < 8.2(1)°); unit B, instead, in an oblique fashion, with a slanting angle of ca. 29.1(1)°. Besides completing the coordination scheme in a closed fashion and thus inhibiting the polymerization of the dinuclear species, the anions provide the necessary charge balance avoiding in this way the need of any external counterion, in contrast to the polymeric bpmu complexes reported in the literature [1,2,4]. In spite of the strain usually imposed by chelation, the flexibility of the intervening ligands allows a rather regular chromophore for copper, with expected 180° angles in the range 170.46(12)–176.92(12)° and expected 90° ones

spanning 82.9(1)–96.8(1)°. An analysis of bond distances allows to singularize the O(1B)–Cu1–N(1D) line as the apical one, with the peculiarity of being shorter than basal ones (mean values, 1.985(30) and 2.150(15) Å, respectively). This oblate shape of the copper polyhedron due to a Jahn Teller contraction is rather unusual and only found in less than 5% of all Cu(O/N)₆ octahedra in the literature (CSD, 2004).

The fact that the binuclear unit is generated through a twofold rotation ensures that both metallic centers bear the same chirality, that is, the two copper(II) ions of one dimer molecule have either a ΔΔ or ΛΛ configuration. These dimers, in turn, stack one on top of the other to form columns parallel to *b*, in a translational operation which also keeps the chirality unchanged. The resulting broad columns (or strips) are therefore characterized by one specific handedness and are opposite to those related to them by the symmetry center. In both types of columns, the bpmu ligands bind having their urea C=O axis colinear and coincident with the twofold axis, and the dimers stack in the same way preserving this leading direction. Thus, two double very strong N–H···O···H–N bonds arise (Fig. 1), one of them intradimeric across the cyclic dimer (Fig. 1, heavy broken lines: N(2D)–H(2DA)···O(1C) [30]), the other one linking dimers

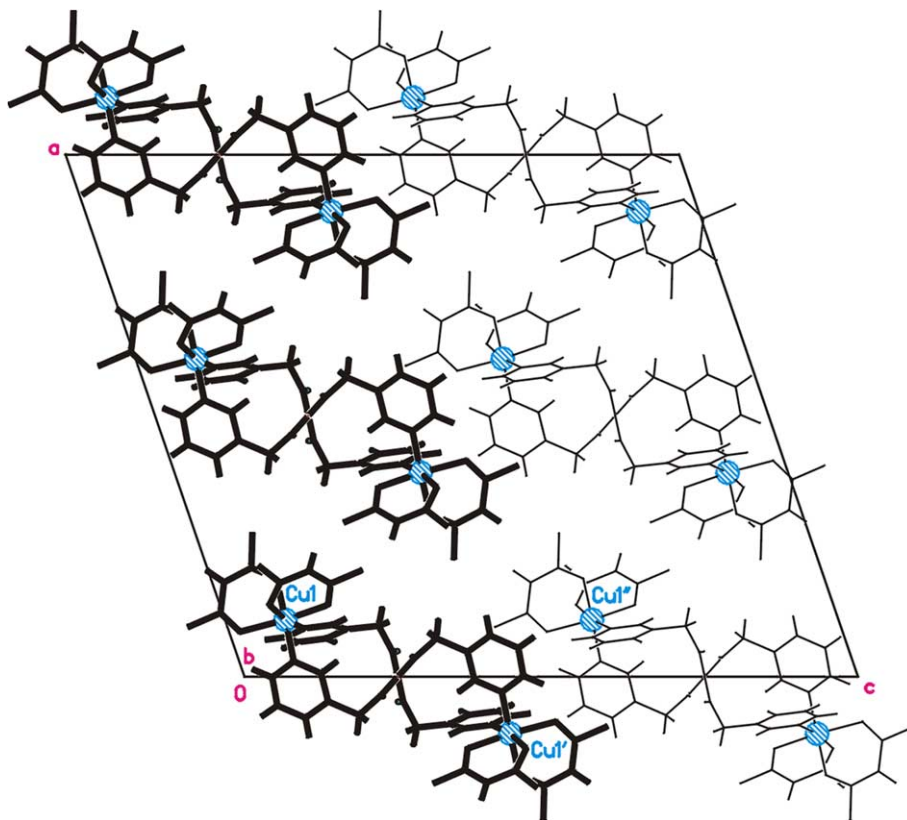


Fig. 2. Packing view of the structure of the metallacycle [Cu(hfac)₂(bpmu)]₂ down the *b*-axis, showing the disposition of the strips in planes of different chirality, represented in heavy and light lining, respectively. Fluorine atoms not represented for clarity (symmetry codes: $-x, y, 1/2 - z$; $x, -y, -1/2 + z$ (or $x, 1 - y, -1/2 + z$, superposed in the figure)).

together into an infinite 1D array along *b* (Fig. 1, double broken lines: N(2C)–H(2CA)···O(1D)#2 [30]). These are the main non-bonding interactions in the structure determining the columnar units for packing. Due to the *C* cell centering, the two types of columns organize segregating themselves into “opposite handed” planes parallel to (0 0 1) (Fig. 2) and individually stabilized through weak C–H···F contacts involving the disordered terminal fluorines, viz., C(3A)–H(3AA)···F(1A5)#3 (intracolumn [31]), C(6C)–H(6CA)···F(1A2)#2 and C(3D)–H(3DA)···F(1B6)#4 (intercolumn [31]). There are also some weaker contacts of the same type linking opposite planes (C(2D)–H(2DB)···F(5A4)#5 [31]), providing for structure stabilization.

A final peculiarity of the packing is that the inter-dimeric Cu...Cu distance is not the shortest one in the structure: the very long bridges subtended by the bpmu ligands set the cations so far apart in the dimer (Cu1...Cu1' in Fig. 2, at 11.195(1) Å), this distance results far larger than, for example, the intercolumnar Cu...Cu [–*x*, –*y*, –*z*] or Cu...Cu [–*x*, 1 – *y*, –*z*] separations (Cu1'...Cu1'' in Fig. 2, 7.263(1), 8.196(1) Å apart) or the intracolumnar one between adjacent dimers, Cu...Cu [*x*, *y* + 1, *z*] (the distance between any copper atom in Fig. 2 and its symmetry related one by an upwards/downwards unit cell translation is 9.042(1) Å).

The above results reveal the permanence of the prearranged hydrogen bonded pattern provided for the bpmu tecton through the O=C(N–H)₂···O=C moieties. The intramolecular and intermolecular repeat distances (4.506(1) and 4.535(1) Å, respectively, Scheme 2) are in the expected range for urea-based derivatives [32]. Consequently, this indicates the prevalence of the H-bonds strength over the steric effect of the bulky {Cu(hfac)₂} fragments, hampering the polymerization but allowing the formation of the discrete compound [Cu(hfac)₂(bpmu)]₂. Thus, by properly tuning the metal–ligand system this approach could serve for controlling the formation of either discrete or infinite supramolecular structures.

Acknowledgments

We are grateful to the Universidad de La Frontera for financial support (Proyecto DIUFRO 120416), CONICYT-FONDAP (project 11980002) for the purchase of a CCD detector and the Spanish Research Council (CSIC) for provision of a free-of-charge license to the CSD system.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.inoche.2005.03.018.

References

- [1] C.L. Schauer, E. Matwey, F.W. Fowler, J.W. Lauher, *J. Am. Chem. Soc.* 119 (1997) 10245.
- [2] C.L. Schauer, E. Matwey, F.W. Fowler, J.W. Lauher, *Cryst. Eng.* 1 (1998) 213.
- [3] G.R. Desiraju, *Angew. Chem., Int. Edit. Engl.* 34 (1995) 2311.
- [4] M.J. Plater, B.M. de Silva, J.M.S. Skakle, R.A. Howie, A. Riffat, T. Gelbrich, M.B. Hursthouse, *Inorg. Chim. Acta* 325 (2001) 141.
- [5] H.W. Roesky, M. Andruh, *Coord. Chem. Rev.* 236 (2003) 91.
- [6] S. Karasawa, M. Tanaka, N. Koga, H. Iwamura, *Chem. Commun.* (1997) 1359.
- [7] M.J. Plater, M.R.St.J. Foreman, A.M.Z. Slawin, *Inorg. Chim. Acta* 303 (2000) 132.
- [8] H.-Y. Shen, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan, B.-W. Sun, G.-L. Wang, X.-K. Yao, H.-G. Wang, *Polyhedron* 17 (1998) 1953.
- [9] Y.-B. Dong, M.D. Smith, R.C. Layland, H.-C. zur Loye, *Inorg. Chem.* 38 (1999) 5027.
- [10] F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang, *J. Am. Chem. Soc.* 123 (2001) 7740.
- [11] R. Horikoshi, T. Mochida, H. Moriyama, *Inorg. Chem.* 40 (2001) 2430.
- [12] Md.B. Zaman, K.A. Udachin, J.A. Ripmeester, *Cryst. Eng. Commun.* 4 (2002) 613.
- [13] Md.B. Zaman, M.D. Smith, D.M. Curtin, H.-C. zur Loye, *Inorg. Chem.* 41 (2002) 4895.
- [14] S.R. Seidel, F.M. Tabellion, A.M. Arif, P.J. Stang, *Israel J. Chem.* 41 (2001) 149.
- [15] S. Karasawa, Y. Sano, T. Akita, N. Koga, T. Itoh, H. Iwamura, P. Rabu, M. Drillon, *J. Am. Chem. Soc.* 120 (1998) 10080.
- [16] Y. Sano, M. Tanaka, N. Koga, K. Matsuda, H. Iwamura, P. Rabu, M. Drillon, *J. Am. Chem. Soc.* 119 (1997) 8246.
- [17] R. Horikoshi, T. Mochida, H. Moriyama, *Inorg. Chem.* 41 (2002) 3017.
- [18] G. Mago, M. Hinago, H. Miyasaka, N. Matsumoto, H. Okawa, *Inorg. Chim. Acta* 254 (1997) 145.
- [19] W.W. Ellis, M. Schmitz, A. Arif, P.J. Stang, *Inorg. Chem.* 39 (2000) 2547.
- [20] K. Matsuda, K. Takayama, M. Irie, *Chem. Commun.* (2001) 363.
- [21] F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang, *Angew. Chem., Int. Ed.* 40 (2001) 1529.
- [22] F.M. Tabellion, S.R. Seidel, A.M. Arif, P.J. Stang, *J. Am. Chem. Soc.* 123 (2001) 11982.
- [23] A methanol solution (3 ml) of bpmu (0.024 g, 0.10 mmol) was added into a solution of Cu(hfac)₂·H₂O (0.050 g, 0.10 mmol) in methanol (3 ml). The resultant green mixture was filtered and upon standing during 24 h green crystals were obtained. The solid was washed at room temperature with methanol (3 × 1 ml) and dried in vacuo. The separated crystals were suitable for X-rays structure determination. Yield: 0.051 g (70.8%). Anal. Calc. for C₂₃H₁₆Cu₁F₁₂N₄O₅: C, 38.37; H, 2.24; N, 7.78. Found: C, 38.37; H, 2.70; N, 7.54.
- [24] Crystal data for the compound [Cu(hfac)₂(bpmu)]₂: C₂₃H₁₆CuF₁₂N₄O₅, *M_r* = 719.94, *T* = 299(2) K, λ (Mo Kα) = 0.71073 Å, monoclinic, space group *C2/c*, *a* = 24.524(3) Å, *b* = 9.0415(8) Å, *c* = 27.253(3) Å, β = 108.898(3)°, *V* = 5717.3(10) Å³, *Z* = 8, *D_c* = 1.673 Mg/m³, μ = 0.883 mm^{−1}, *F*(0 0 0) = 2872, 21138 reflections collected (1.58° < θ < 28.05°), 6425 unique [*R*(int) = 0.063], GOF: 0.881, *R* indices [*I* > 2σ (*I*): *R*₁ = 0.0575, *wR*₂ = 0.1547, largest diff. peak and hole: 0.596/−0.279 e Å^{−3}. Data were collected on a Bruker AXS SMART APEX CCD diffractometer with SMART [25] as the driving software; data integration was performed using SAINT [26] and a semi-empirical absorption correction applied. The structure was solved by direct methods and difference Fourier, and refined by least squares on *F*² with anisotropic displacement parameters for

non-H atoms. All the hydrogen atoms were defined by the stereochemistry and accordingly placed at their calculated positions and allowed to ride onto their host carbons both in coordinates as well as thermal parameters [$U_{\text{iso}}(\text{H}) = 1.2 * U_{\text{eq}}(\text{Host})$]. All calculations to solve the structures, refine the models proposed and obtain derived results were carried out with the computer programs SHELXS97 and SHELXL97 [27] and SHELXTL/PC [28]. Full use of the CCDC package was also made for searching in the CSD Database [29]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 259383 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

- [25] Bruker, SMART-NT V5.624. Data Collection Software, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 2001.
- [26] Bruker, SAINT-NT V6.02a. Data Reduction Software, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 2000.
- [27] G.M. Sheldrick, SHELXS-97 and SHELXL-97. Programs for Structure Resolution and Refinement, Univ. of Göttingen, Germany, 1997.
- [28] G.M. Sheldrick, SHELXTL-PC. Version 5.0 Siemens, Analytical X-ray Instruments Inc., Madison, WI, USA, 1994.
- [29] F.H. Allen, Acta Cryst. B 58 (2002) 380–388.
- [30] Hydrogen bonds N–H···O (Å and °): N(2D)–H(2DA)···O(1C) [$d(\text{N–H}) = 0.86$, $d(\text{H···O}) = 2.04$, $d(\text{N···O}) = 2.816(5)$, $\angle(\text{NHO}) = 149.4$], N(2C)–H(2CA)···O(1D)# [$d(\text{N–H}) = 0.86$, $d(\text{H···O}) = 2.09$, $d(\text{N···O}) = 2.826(5)$, $\angle(\text{NHO}) = 143.5$]. Symmetry transformations used to generate equivalent atoms: #2 $x, y - 1, z$. Values involving calculated hydrogens quoted without esd's.
- [31] Hydrogen bonds C–H···F (Å and °): C(3A)–H(3AA)···F(1A5)#3 [$d(\text{C–H}) = 0.93$, $d(\text{H···F}) = 2.64$, $d(\text{C···F}) = 3.37(2)$, $\angle(\text{CHF}) = 136.5$], C(6C)–H(6CA)···F(1A2)#2 [$d(\text{C–H}) = 0.97$, $d(\text{H···F}) = 2.56$, $d(\text{C···F}) = 3.44(5)$, $\angle(\text{CHF}) = 151.4$], C(3D)–H(3DA)···F(1B6)#4 [$d(\text{C–H}) = 0.93$, $d(\text{H···F}) = 2.35$, $d(\text{C···F}) = 3.27(2)$, $\angle(\text{CHF}) = 172.2$], C(2D)–H(2DB)··· F(5A4)#5 [$d(\text{F–H}) = 0.93$, $d(\text{H···F}) = 2.52$, $d(\text{C···F}) = 3.11(3)$, $\angle(\text{CHF}) = 122.1$]. Symmetry transformations used to generate equivalent atoms: #2 $x, y - 1, z$ #3 $-x + 1/2, y + 1/2, -z + 1/2$ and #4 $x - 1/2, y + 1/2, z$ #5 $-x, -y + 1, -z$. Values involving calculated hydrogens quoted without esd's.
- [32] X. Zhao, Y.-L. Chang, F.W. Fowler, J.W. Lauher, J. Amer. Chem. Soc. 112 (1990) 6627.