Dimeric Metallo-Organic Supramolecular Quinoxaline Stacking Synthons

Fenton Heirtzler,*[a][‡] Sandra Dias,[a] and Markus Neuburger[b]

Keywords: Supramolecular chemistry / Helical structures / Heterocycles / Stacking interactions / Self-assembly / Sandwich complexes

Condensation of *ortho*-phenylene diamines with an unsymmetrical 2,6′-bipyridyl-2′′-pyridyl α-diketone (**2**) affords helical ligands **3a** and **3b** that self-assemble in the presence of copper(I) to produce the helical, dimeric metallo-organic complexes [$\mathbf{3a}_2Cu_2$][PF_6]$_2$ and [$\mathbf{3b}_2Cu_2$][PF_6]$_2$. These complexes have a flat, double-decker-like structure that results from atopomeric twisting in the ligand scaffolding, as confirmed by X-ray crystal structural analysis on [$\mathbf{3a}_2Cu_2$][PF_6]$_2$. This study also indicates a close parallel between the distances involved in inter- and intramolecular stacking phenomena. Detailed NMR spectroscopic analysis of both complexes indicates that their dications possess very closely related solution-state structures. Achieving this self-assembly program is an important step towards realizing dimerically self-assembled metallo-organic materials that have a discotic alignment.

Introduction

Oligopyridines and related compounds self-assemble in the presence of appropriate metal ions into tubular metallo-organic complexes with either a helical chirality[1] or a *meso*-configuration.[2] Ligands of less regular structure may form dimeric complexes with a flattened topology.[3] Our work concerns the synthesis[4] and metallo-organic supramolecular chemistry of hybrid pyrazine−pyridine ligands. These are 2,3-disubstituted with 2,6′-substituted oligopyridyl chains. In the presence of appropriate metal cations, they self-assemble to dimeric, intramolecularly stacked metallo-organic complexes.[5] Pyrazine derivatives of 2,5-disubstituted ligands with oligopyridyl chains undergo other metallo-organic self-assembly patterns.[6] Nevertheless, knowledge of the precise manner in which the structures of the 2,3-disubstituted ligands control their self-assembly behavior is limited. Solution- and solid-state studies have indicated that torsional congestion leads to helical twisting of the oligopyridyl strands about each other, and inter- and intramolecular π-stacking interactions occur in both the ligands and their complexes.[4b]

In the presence of copper(I), unsymmetrical ligand **1** forms a dimeric cation [$\mathbf{1}_2Cu_2$]$^{2+}$, which in principle may exist in either C_2-symmetric or *meso* configurations. In the C_2-form, pairs of pyrazine and pyridine rings overlap, whereas in the *meso* form two pyrazine−pyridine overlaps occur. However, only the chiral form of [$\mathbf{1}_2Cu_2$]$^{2+}$ has been detected. These double-decker dimers can also be arranged in stacked fashion in the crystal lattice.[5b] Thus, we were attracted to the use of related compounds to construct parallel metallo-organic π-stacking arrays, in particular those possessing discotic and lamellar ordering. Discotic macroscopic ordering is conductive to the formation of mesophase-forming, liquid-crystalline materials and facilitates their use in liquid-crystalline displays and electrically and photoelectrically conductive films.[7] The tetrahedral geometry of copper(I) hitherto has resulted in nematic (tubular) mesotropic ordering in oligopyridine-type metallo-organic complexes.[8]

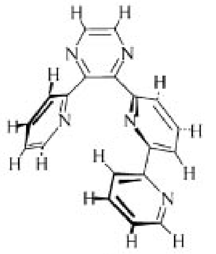
Initial steps towards these goals include: (a) the preparation of ligands resembling **1** but containing long hydrophobic chains and (b) confirmation of the ligands' self-assembly pattern and stereochemistry {c.f. [$\mathbf{1}_2Cu_2$]$^{2+}$, C_2 or *meso*}. Ligand **1** is synthesized from α-diketone **2**, and we have presented a synthesis of **2** that is amenable to multigram amounts.[4b] Thus, simple condensation of **2** with aromatic 1,2-diamines already containing attachment points for hydrocarbon tails will afford quinoxaline-type ligands analogous to **1**. We chose attachment of alkyl groups through ether bonding because of this linkage's chemical robustness. An additional benefit of the overall strategy is the extension of the π-electronic stacking system to enhance graphite-like stacking interactions in the corresponding dimeric complexes.

---

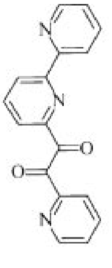
[a] Chemical Laboratory, School of Physical Sciences, University of Kent,
Canterbury, Kent CT2 7NZ, UK
[b] Departement Chemie, Universität Basel,
Spitalstrasse 51, 4056 Basel, Switzerland
Fax: (internat.) +41-61-267-1005
E-mail: markus.neuburger@unibas.ch
[‡] New address: Department of Entomology, University of California,
Davis, CA 95616 USA.
Fax: (internat.) + 1-530-752-1537,
E-mail: Heirtzler@web.de

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200300531



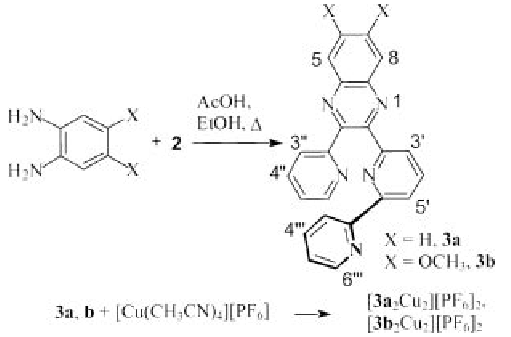
1



2

Results and Discussion

The α-diketone **2** was condensed under acidic conditions with *ortho*-phenylene diamine or 4,5-diaminoveratrole,[9] affording the unsymmetrical quinoxaline-pyridine **3a** and the dimethoxyquinoxaline homologue **3b** in 47 % and 48 % yields, respectively (Scheme 1).[10] The ^{1}H NMR spectra (Figure 1) of these two materials were completely assigned through combination of 2D techniques and comparison of the quinoxaline AA′BB′ systems. Just as for **1**, compounds **3a** and **3b** experience an upfield shifting of H-3′′′ attached to the terminal pyridine ring of the bipyridyl ring system (δ = 7.30 ppm), which is attributed to through-space interaction with the opposing solitary pyridine ring and a helical molecular conformation.



Scheme 1. Synthesis of quinoxaline-type ligands and their dimeric copper(I) complexes

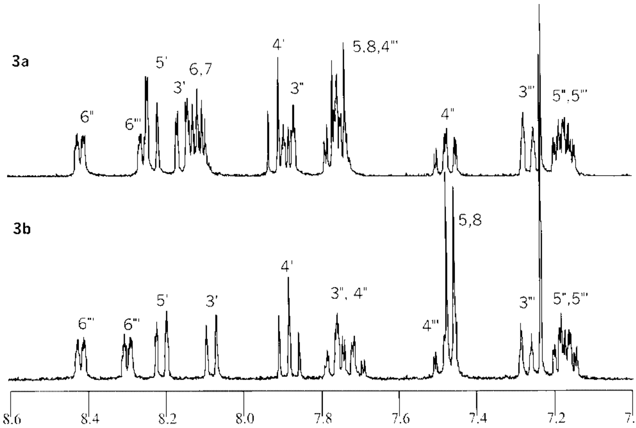


Figure 1. ^{1}H NMR spectra of ligands **3a** and **3b** ($CDCl_3$, 270 MHz)

Treatment of ligands **3a** and **3b** with one equivalent of copper(I)tetrakis(acetonitrilo) hexafluorophosphate in degassed methanol at room temperature gave purple-colored solutions, from which solids were deposited. Crystalline material resulted after slow diffusion of diethyl ether into concentrated acetonitrile solutions. Results of combustion analyses and electrospray mass spectrometry together indicated the presence of dimeric complexes $[\mathbf{3a}_2Cu_2][PF_6]_2$, and $[\mathbf{3b}_2Cu_2][PF_6]_2$.[11] The differential scanning calorimetric profiles of these two materials contain sharp endotherms at 329 and 250 °C, respectively, consistent with unitary compositions. Relative to the parent ligands, their UV-Vis spectra exhibit intensely absorbing, red- and blue-shifted maxima, as well as weak MLCT bands occurring at λ_{max} = 510 nm $\{[\mathbf{3a}_2Cu_2][PF_6]_2,\ \varepsilon = 4.000\}$ and 479/580 nm $\{[\mathbf{3b}_2Cu_2][PF_6]_2,\ \varepsilon = 6.100/4.000\}$. The latter complex also displays strong adsorption bands at 353/368 nm, attributable to the dimethoxyquinoxaline chromophore (c.f. ligand **3b**: 362/387 nm). The presence of the MLCT bands in both complexes bespeaks of the existence of copper(I) centers surrounded by tetrahedral ligand fields. Yet, the lack of exceptional concentration dependence in the position of the λ_{max} values bespeaks of the absence of a pronounced solution-state aggregation.[12] The complexes were also investigated with cyclic voltammography (Figure 2). In particular, $[\mathbf{3a}_2Cu_2][PF_6]_2$ and $[\mathbf{3b}_2Cu_2][PF_6]_2$ display quasi-reversible Cu(I/II) processes centered at 0.44 V and 0.38 V, relative to the ferrocene/ferrocenium couple. Both metal centers within the same complex are active at identical potentials. Repeated redox cycling of the quinoxaline derivative complex resulted in the decomposition of this material, as evidenced by the appearance of additional redox processes at 1.04 V (reduction) and 0.48 V (oxidation). Gratifyingly, these processes were significantly less prominent in $[\mathbf{3b}_2Cu_2][PF_6]_2$. Since the introduction of electron-rich methyl ether groups into the ligand scaffolding should increase the ligand sensitivity to oxidative degradation, it is possible that greater ligand−metal interaction may account for the stability of $[\mathbf{3b}_2Cu_2][PF_6]_2$.

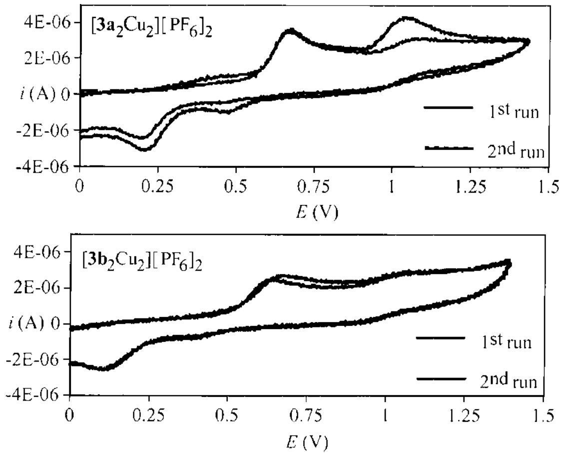


Figure 2. Cyclic voltammograms of dimeric dicopper(I) complexes in acetonitrile (supporting electrolyte: nBu$_4$PF$_6$; all potentials relative to the ferrocenium−ferrocene couple)

The ^1H NMR spectra of both complexes were completely assigned through use of 2D NMR spectroscopy and by comparison to related compounds[13] (Figure 3). The chemical shifts of the flanking 2,6′-bipyridyl groups for both complexes are generally coincident. The proton shifts attributed to the pyridine ring participating in the metallophane "decks" appear upfield as expected from their local anisotropy. In [**3b**$_2$Cu$_2$][PF$_6$]$_2$, the aromatic positions adjacent to the methoxy groups appear at δ = 6.6/6.8 ppm, which we tentatively interpret as evidence of a mutual shielding effect between the two equivalents of disubstituted quinoxaline-like complexes. Of special note in both complexes is the shielding effect on H-3′′, which is attributable to an orthogonal π-stacking interaction with the bipyridyl ring system (c.f. H-3′′′ in **3a** and **3b**). Variable temperature NMR spectra, recorded in [D$_3$]MeCN and non-coordinating [D$_3$]MeNO$_2$ [14] down to −40 °C, exhibited negligible decoalescence phenomena. It is thus reasonable to assume that [**3a**$_2$Cu$_2$][PF$_6$]$_2$ and [**3b**$_2$Cu$_2$][PF$_6$]$_2$ possess similar structures in solution.

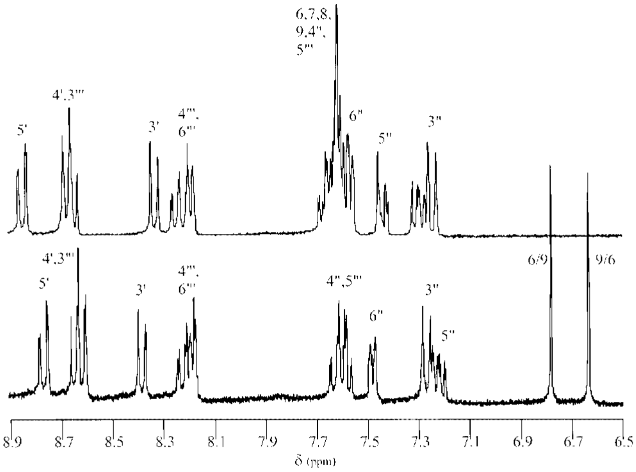


Figure 3. ^1H NMR Spectra of dicopper(I) metallophanes [**3a**$_2$Cu$_2$][PF$_6$]$_2$ and [**3b**$_2$Cu$_2$][PF$_6$]$_2$ (CD$_3$CN, 270 MHz)

A crystal structure analysis was undertaken on the complex [**3a**$_2$Cu$_2$][PF$_6$]$_2$ to investigate its stereochemistry and lattice packing.[15] A double-decker geometry results from the combination of two bidentate sites (2,6′-bipyridyl and 2′,3"-pyridylquinoxalinyl) surrounding each tetrahedral metal center. Quinoxaline N adjacent to bipyridyl remains uncoordinated. While this arrangement is shared by both the *C*$_2$- and *meso*-diastereomers, the dication crystallizes in the *C*$_2$-symmetric form, that is, pyridyl quinoxaline moieties within the same dication are arranged in a parallel fashion. The overall crystal symmetry (space group *Pbca*) corresponds to a racemic crystal; one of the two equally likely enantiomers is displayed in Figure 4.

Intramolecularly, the quinoxaline ring fragments overlap in an offset fashion (Figure 5). This also results in classical parallel π-stacking overlap[16] between areas of low and high electron density. The geometrical center of the benzenoid subring on quinoxaline is separated from quaternary C(8a) by 3.45 Å, while the center of the pyrazinoid ring is closest to C(4a) at 3.40 Å. The stacked quinoxalinyl ring system is twisted by 18.67° relative to pyridyl. A consequence of this is that while the quinoxaline ring atoms are separated from the mean plane of the opposing quinoxaline ring by 3.36 ± 0.04 Å, the average atomic separation from the pyridylquinoxaline system to its opposing mean plane is 3.43 ± 0.16 Å. The two quinoxalinyl fragments deviate by 1.3° from coplanarity, while the two stacked pyridyl residues the deviation is 5.9°.

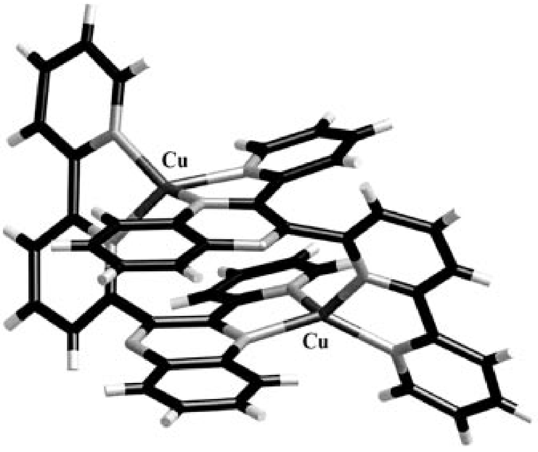


Figure 4. X-ray crystal structure of one of the two enantiomeric dicopper(I) cations from [**3a**$_2$Cu$_2$][PF$_6$]$_2$

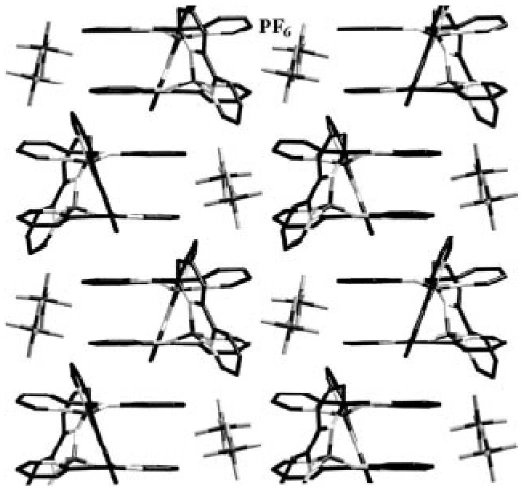


Figure 5. Crystal lattice of [**3a**$_2$Cu$_2$][PF$_6$]$_2$

Homochiral dicationic complexes interact through offset stacking interactions involving the quinoxaline ring systems (average distance of quinoxaline atoms from the mean plane, 3.35 ± 0.09 Å; dihedral angle between planes: 3.90°); in particular those involving benzo and pyrazinyl domains overlap (distance between ring centers, 3.63 Å). Strata composed of Δ,Δ- and Λ,Λ−configured metallophane dimers are separated by weaker parallel edge-on contacts between 2,2′-bipyridyl flanks (ca. 4.8 Å) and the hexafluorophosphate counterions.

Conclusion

The applicability of quinoxaline-pyridine hybrids for engineering highly stacked, self-assembling metallo-organic networks has been confirmed. It employs a combination of heterocyclic synthesis, a new metallo-organic supramolecular synthon and intramolecular π-stacking effects over extended arene surfaces. At least for smaller alkoxy chains, a consequence of the complexes' C_2-symmetry is the location of all four ether functionalities on the same side of the complex dication. The extension of this strategy to the preparation of mesotropic, liquid-crystalline materials is currently under investigation.

Acknowledgments

We thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support (Grant R/R09138), the EPSRC Mass Spectroscopy Centre for mass spectra as well as Dr. D. Smith (University of Kent) for technical assistance.

---

[1] [1a] L. F. Lindoy, I. M Atkinson, in *Self-Assembly in Supramolecular Systems-Monographs* in *Supramolecular Chemistry* (Ed.: J. F. Stoddart), Royal Society of Chemistry, London, **2000**. [1b] J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, New York, VCH, **1995**.

[2] [2a] M. Albrecht, S. Kotila, *Chem. Commun.* **1996**, 2309−2310. [2b] A. Bilyk, M. M. Harding, P. Turner, T. W. Hambley, *J. Chem. Soc., Chem. Commun.* **1995**, 2549−2553. [2c] M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun.* **1997**, 307−308.

[3] [3a] P. Baxter, J.-M. Lehn, A. DeCian, J. Fischer, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 69−72. [3b] M. Fujita, N. Fujita, K. Ogura, K. Yamaguchi, *Nature* **1999**, *400*, 52−55. [3c] A. H. Eisenberg, M. V. Ovchinnikov, C. A. Mirkin, *J. Am. Chem. Soc.* **2003**, *125*, 2836−2837.

[4] [4a] F. R. Heirtzler, M. Neuburger, M. Zehnder, E. C. Constable, *Liebigs Ann./Recueil* **1997**, 297−301. [4b] F. Heirtzler, M. Neuberger, K. Kulike, *J. Chem. Soc., Perkin Trans. 1* **2002**, 809−820.

[5] [5a] F. Heirtzler, T. Weyhermüller, *J. Chem. Soc., Dalton Trans.* **1997**, 3653−3654. [5b] T. Bark, T. Weyhermüller, F. Heirtzler, *Chem. Commun.* **1998**, 1475−1476.

[6] [6a] T. Bark, M. Duggeli, H. Stoeckli-Evans, A. v. Zelewsky, *Angew. Chem. Int. Ed.* **2001**, *40*, 2848−2851. [6b] D. Brown, S. Muranjan, Y. Jang, T. Thummel, *Org. Lett.* **2002**, *4*, 1253−1256.

[7] [7a] J.-P. Farges in *Organic Conductors -Fundamentals and Applications* (Ed.: A. M. Hermann), Marcel Dekker, New York, **1994**. [7b]E. O. Arikainen, N. Boden, J. Bushby, J. Clements, B. Movaghar, A. Wood, *J. Mater. Chem.* **1995**, *5*, 2161−2165. [7c] W. B. Euler in *Handbook of Organic Conductive Molecules and Polymers* (Ed.: H. S. Nalwa), Chichester, Wiley, **1997**, vol. 2, p 719. [7d] T. Ishiguro, K. Yamaji, G. Saito in *Organic Superconductors -Springer Series in Solid State Sciences*, vol. 88 (Ed.: P. Fulde), Springer-Verlag, Heidelberg, **1998**.

[8] [8a] L. Douce, A. El-ghayoury, A. Skoulios, R. Ziessel, *Chem. Commun.* **1999**, 2033−2034. [8b] K. E. Rowe, D. W. Bruce, *Liq. Cryst.* **1996**, *20*, 183−193. [8c] C. Tschierske, *Angew. Chem. Int. Ed.* **2000**, *39*, 2454−2458. [8d] E. Terazzi, J. M. Benech, J. P. Rivera, G. Bernardinelli, B. Donnio, D. Guillon, C. Piguet, *Dalton Trans.* **2003**, 769−772.

[9] M. M. G. Antonisse, B. H. M. Snellink-Ruel, I. Yigit, J. F. J. Engbersen, D. N. Reinhoudt, *J. Org. Chem.* **1997**, *62*, 9034−9038.

[10] Full experimental details for the preparation of **3a**, **3b**, $[\mathbf{3a}_2\mathrm{Cu}_2][\mathrm{PF}_6]_2$ and $[\mathbf{3b}_2\mathrm{Cu}_2][\mathrm{PF}_6]_2$, including ^{1}H and ^{13}C NMR, IR, UV-Vis spectroscopy (Figures, mass spectra and combustion analyses are provided as Supporting information).

[11] $[\mathbf{3a}_2\mathrm{Cu}_2][\mathrm{PF}_6]_2$: $\mathrm{C}_{46}\mathrm{H}_{30}\mathrm{Cu}_2\mathrm{F}_{12}\mathrm{N}_{10}\mathrm{P}_2\cdot 2\mathrm{H}_2\mathrm{O}$ (1175.86): calcd. C 46.99, H 2.91, N 11.91; found C 46.70, H 2.63, N 11.55. LSIMS (NOBA matrix, rel. intensity): $m/z = 993$ $\{[\mathrm{M} - \mathrm{PF}_6]^+$, 25 %}, 849 $\{[\mathrm{M} - 2\mathrm{PF}_6]^+$, 75 %}; $[\mathbf{3b}_2\mathrm{Cu}_2][\mathrm{PF}_6]_2$: $\mathrm{C}_{50}\mathrm{H}_{38}\mathrm{Cu}_2\mathrm{F}_{12}\mathrm{N}_{10}\mathrm{O}_4\mathrm{P}_2\cdot \mathrm{H}_2\mathrm{O}$ (1277.95): calcd. C 46.99, H 3.16, N 11.96; found C 47.40, H 3.61, N 11.50. MALDI-TOF (MeOH/MeCN, rel. intensity): $m/z = 1113$ $\{[\mathrm{M} - \mathrm{PF}_6]^+$, 25 %}, 484 $\{[\mathrm{M}/2 - 2\mathrm{PF}_6]^+$, 100 %}.

[12] C. A. Hunter, P. Leighton, J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1* **1989**, 547−552.

[13] The details of these studies will be reported shortly (I. Prokes, F. Heirtzler, *Chem. Commun.* **2003**, *in press*).

[14] W. A. E. McBryde, *IUPAC Chemical Data Series, no. 17*, Pergamon Press: Oxford, **1978**.

[15] X-ray Crystallographic Study on $[\mathbf{3a}_2\mathrm{Cu}_2][\mathrm{PF}_6]_2$: A sample was mounted on a KappaCCD area detector using the oil-drop method. Unit cell determination, data collection and integration was carried out with the programs Collect,[17] Denzo and Scalepack.[18] The structure was solved by direct methods using the program SIR92.[19] Anisotropic least-squares full-matrix refinement was carried out on all non-hydrogen atoms using the program CRYSTALS.[20] Positions of the hydrogen atoms were determined geometrically. Chebychev polynomial weights[21] were used to complete the refinements. Scattering factors have been taken from the International Tables, vol. IV, Table 2.2B. Crystallographic data for $[\mathbf{3a}_2\mathrm{Cu}_2][\mathrm{PF}_6]_2$ ($\mathrm{C}_{46}\mathrm{H}_{30}\mathrm{Cu}_2\mathrm{N}_{10}\cdot 2\mathrm{PF}_6$): $M_r = 1139.83$ gmol^{-1}, brown needles ($0.12 \times 0.18 \times 0.41$ mm), space group *Pbca*, $a = 13.4184(16)$, $b = 24.736(6)$, $c = 27.549(5)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 9143.9$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd.}} = 1.679$ g·cm^{-3}, $F(000) = 4464$, radiation Mo-K_α ($\lambda = 0.70173$ Å), $T = 173$ °C, 78945 reflections measured ($4.08 < \theta < 27.50$) of which 10477 were independent. $R1 = 0.0686$, $wR2 = 0.0498$, goodness-of-fit: 0.9872 for 6220 reflections with $I > 2\sigma(I)$ and 658 parameters. Residual electron density: $-0.84/1.03$ e·Å^{-3}. CCDC-216375 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[16] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.

[17] COLLECT Software, Nonius BV **1997−2001**.

[18] Z. Otwinowski and W. Minor, in *Methods in Enzymology* in *Macromolecular Crystallography*, vol. 276, Part A (Eds.: C. W. Carter, Jr. and R. M. Sweet) Academic Press, New York, **1997**, p 307.

[19] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435.

[20] D. J. Watkin, R. J. Carruthers, P. Betteridge, CRYSTALS, Chemical Crystallography Laboratory, Oxford, UK, **1985**.

[21] J. R. Carruthers, D. J. Watkin, *Acta Crystallogr., Sect. A* **1979**, 698−699.

Received July 31, 2003