A meso-Helical Coordination Polymer from Achiral Dinuclear $[Cu_2(H_3CCN)_2(\mu\text{-pydz})_3][PF_6]_2$ and 1,3-Bis(diphenylphosphanyl)propane—Synthesis and Crystal Structure of ${}^{1}_{\infty}\{[Cu(\mu\text{-pydz})_2][PF_6]\}$ (pydz = pyridazine)

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Dedicated to Professor Georg Süss-Fink

Abstract: Reaction of achiral $[Cu_2(H_3CCN)_2(\mu\text{-pydz})_3][PF_6]_2$ (**1**) (pydz = pyridazine) with bidendate 1,3-bis(diphenylphosphanyl)propane (**2**) in acetonitrile at room temperature in a 1:1 ratio yielded the mononuclear copper(I) complex $[Cu\{CH_2(CH_2PPh_2)_2\}_2][PF_6]$ (**3**) together with new one-dimensional coordination polymer ${}^{1}_{\infty}\{[Cu(\mu\text{-pydz})_2][PF_6]\}$ (**4**). Air-sensitive single crystals of **4**, suitable for X-ray structure determination, were grown from a mixture of dichloromethane/hexane [crystal system: monoclinic; space group: $C2/c$; $a = 21.910(3)$, $b = 12.130(2)$, $c = 25.704(3)$ Å, $\beta = 110.08(10)^\circ$, $V = 6416.65(16)$ Å^3]. The one-dimensional coordination polymer ${}^{1}_{\infty}\{[Cu(\mu\text{-pydz})_2][PF_6]\}$ (**4**) exhibits as outstanding feature the rare structure of a *meso*-helix.

Keywords: coordination polymers · copper · helical structures · *meso* compounds · N ligands · structure elucidation

Introduction

Helical architectures are ubiquitous in nature. The most prominent representatives, depicted here are α-helical polypeptides, double-helical nucleic acids and microtubules. The overall architectural plans required for helix formation are encoded within the molecular building blocks. The most relevant parameters to control the architecture of polymeric helix strands are the topology of the monomers.[1] Six angularly annelated benzene rings form [6]-helicene, poly(*m*-phenylene) displays an helical chain,[2] oligomeric heteroarenes create helical architectures[3] and polymeric isocyanides form helical rigid rods.[4] As a rule, achiral organic building blocks yield racemic mixtures of helices. It is not well understood, however, how homochiral packing of helices in crystals can be induced.[5] A much more interesting possibility is homochiral crystallisation, by which all the crystals display the same chirality as was shown for the helical coordination polymer generated from an achiral anthracene-pyrimidine derivative and cadmium nitrate.[6, 7] Usually, when achiral ligands are treated with appropriate metal ions, one of the two one-dimensional helices in the infinite unit cell is left-handed and the other right-handed.[8]

To date, only a few examples of chiral, non-racemic, helical coordination polymers have been reported in which the chirality is induced by a stereogenic centre[9] or atropisomerism.[10] However, enantiomerically pure *R*/*S* ligands may well generate diastereomeric helical strands [(*R*,*M*)/(*R*,*P*)] or [(*S*,*M*)/(*S*,*P*)], which are present in pairs in the crystal.[11]

Even though *meso*-helices are wide spread in everyday use and in nature, as known for telephone wires and tendrils of a variety of plants, there is little known about *meso*-helical molecules. One interesting organic example is a cycloamylose that consists of 26 glucose units, in which a right- and a left-handed helix are linked to give a cyclic *meso*-helix with two points of contraflexure.[12] To the best of our knowledge, hitherto, only two archetypes of one-dimensional *meso*-helical coordination polymers have been characterised.[13]

Results and Discussion

Air-sensitive one-dimensional coordination polymer **4** was prepared in dry acetonitrile at room temperature together with mononuclear copper(I) complex $[Cu\{CH_2(CH_2PPh_2)_2\}_2][PF_6]$ (**3**)[14] by reaction of equimolar amounts of dinuclear copper(I) complex $[Cu_2(H_3CCN)_2(\mu\text{-pydz})_3][PF_6]_2$ (**1**)[15] (pydz = pyridazine) with 1,3-bis(diphenylphosphanyl)propane, $\{CH_2(CH_2PPh_2)_2\}$ **2**, Scheme 1.

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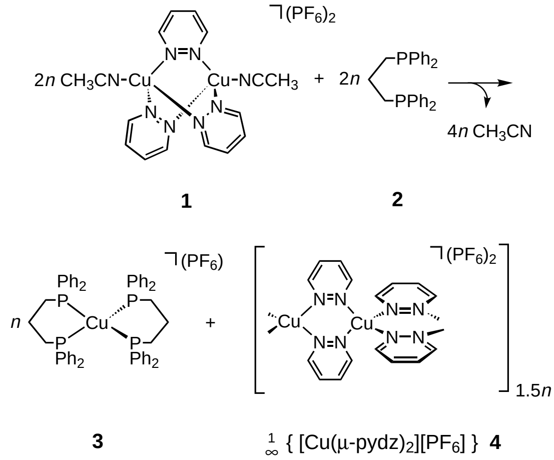


Scheme 1. Synthesis of coordination polymer **4**.

Crystallisation of the yellow powder of polymer **4** from a mixture of dichloromethane/hexane afforded single crystals suitable for X-ray diffraction. The one-dimensional coordination polymer $^{1}_{\infty}\{[\mathrm{Cu}(\mu\text{-pydz})_2][\mathrm{PF}_6]\}$ (**4**) crystallises in the monoclinic space group *C*2/*c* with $a = 21.910(3)$, $b = 12.130(2)$, $c = 25.704(3)$ Å, $\beta = 110.08(10)°$, $V = 6416.65(16)$ Å^3. Crystallographic data and structure refinement details for polymer **4** are summarised in Table 1. Selected bond lengths and angles are listed in Table 2.

Coordination polymer **4** consists of a one-dimensional infinite chain exclusively composed of copper(I) ions bridged by achiral pyridazine ligands. In the crystal, strands of **4** run parallel along the crystallographic *c* axis (Figure 1).

In **4** each copper(I) centre is coordinated by four pyridazine ligands in a *pseudo*-tetrahedral geometry;[16] this creates the unexpected nonlinear structure of **4** (there are two slightly different centres: Cu1 and Cu2; mean bond lengths and angles: Cu−N = 2.04 Å; N-Cu-N = 109.3°) (Figure 2).

Detailed analysis of the one-dimensional infinite framework of **4** revealed that eight copper centres constitute the repeating unit, creating a extraordinary *meso*-helix (Figure 3). Up to now, only a few *meso*-helices are known. Recently, Becker et al. reported on a *meso*-helical structure of a lithium phosphanide polymer.[13] However, polymeric chains prepared from pyridazine as *exo*-bidentate heterocyclic ligands exhibited exclusively classical single-stranded helix structures.[17] *meso*-Helical $^{1}_{\infty}\{[\mathrm{Cu}(\mu\text{-pydz})_2][\mathrm{PF}_6]\}$ (**4**) presents an unprecedented example among pyridazine-based coordination polymers.

Abstract in French: *La réaction entre le complexe achiral* $[\mathrm{Cu_2(H_3CCN)_2(\mu\text{-}pydz)_3}][\mathrm{PF_6}]_2$ (***1***) *(pydz = pyridazine) et la phosphine bidentate 1,3-bis(diphénylphosphine)propane* (***2***) *dans l'acétonitrile, à température ambiante, selon un rapport stoechiométrique 1:1 entraîne la formation du complexe mononucléaire de cuivre(I)* $[\mathrm{Cu\{CH_2(CH_2PPh_2)_2\}_2}][\mathrm{PF_6}]$ (***3***) *ainsi que du nouveau polymère de coordination monodimensionnel* $^{1}_{\infty}\{[\mathrm{Cu}(\mu\text{-pydz})_2][\mathrm{PF}_6]\}$ (***4***)*. Des mono-cristaux de* ***4*** *sensibles à l'air, aptes à la détermination structurale par rayons X ont été obtenus dans un mélange de dichlorométhane/hexane [système cristallin : monoclinique ; groupe spatial : C2/c;* $a = 21.910(3)$, $b = 12.130(2)$, $c = 25.704(3)$ Å, $\beta = 110.08(10)°$, $V = 6416.65(16)$ Å^3*]. Le polymère de coordination mono-dimensionnel* $^{1}_{\infty}\{[\mathrm{Cu}(\mu\text{-pydz})_2][\mathrm{PF}_6]\}$ (***4***) *présente comme remarquable caractéristique, une rare structure de type méso-hélice.*

Table 1. Selected crystallographic and data collection parameters for **4**.

formula	$C_8H_8N_4PF_6Cu$
M_r [g mol^{-1}]	368.7
colour	yellow
size [mm^3]	0.40 × 0.30 × 0.20
crystal system	monoclinic
Space group	*C*2/*c*
a [Å]	21.9103(3)
b [Å]	12.1307(2)
c [Å]	25.7047(3)
α [°]	90
β [°]	110.0810(10)
γ [°]	90
V [Å^3]	6416.65(16)
Z	4
T [K]	173(2)
ρ_{calcd} [mg m^{-3}]	1.878
μ [mm^{-1}]	1.856
F(000)	3584
Θ range [°]	1.69−27.48
index ranges	$-28 \leq h \leq 28$ $-15 \leq k \leq 15$ $-33 \leq l \leq 33$
reflections collected	13278
independent reflections	7298 [R(int = 0.0217]
absorption correction	ψ scan
max/min transmission	0.7078/0.5239
data/parameters	7298/415
goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0497$, w$R2 = 0.1341$
R indices (all data)	$R1 = 0.0674$, w$R2 = 0.1486$
largest diff. peak/hole [e Å^{-3}]	1.171/ − 1.155

Table 2. Selected interatomic distances [Å] and angles for **4**.[a]

Cu1−N12^I	2.001(3)	Cu1−N21	2.022(3)
Cu1−N11	2.068(3)	Cu1−N31	2.033(3)
N11−N12	1.357(4)	N21−N22	1.350(4)
N31−N32	1.361(4)	N21−N26	1.325(5)
N22−N23	1.332(4)	C25−C26	1.380(5)
C23−C24	1.389(6)		
N12^I-Cu1-N21	113.49(11)	N12^I-Cu1-N31	111.21(11)
N21-Cu1-N31	112.93(11)	N12^I-Cu1-N11	117.70(11)
N21-Cu1-N11	102.32(11)	N31-Cu1-N11	98.08(11)
C16-N11-N12	118.6(3)	C16-N11-Cu1	120.9(2)
N12-N11-Cu1	119.7(2)	C13-N12-N11	118.9(3)
N12-C13-C14	124.0(3)	C15-C14-C13	117.3(3)
C14-C15-C16	117.3(3)	N11-C16-C15	123.8(3)

[a] Symmetry transformations (I): $-x$, $-y$, $-z$.

A circle can be converted into a helix simply by transforming it in the third dimension. Similarly, a *meso*-helix is a three-dimensional presentation of a lemniscate (an eight; Figure 4).

The IR spectrum of **4** exhibits characteristic absorptions of the pyridazine ligands at 3056, 1440, 1426 and 762 cm^{-1}. The ^{1}H NMR spectrum displays two broad signals at $\delta = 9.28$ and 7.81, corresponding to the aromatic protons of the pyridazine

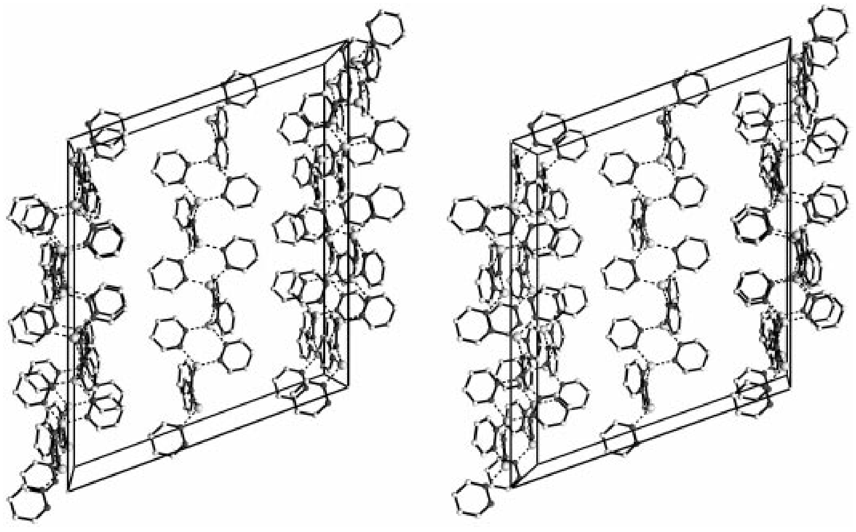


Figure 1. Stereoview along the *b* axis of the crystal packing of **4**. (Solvent molecules and counter ions omitted for clarity).

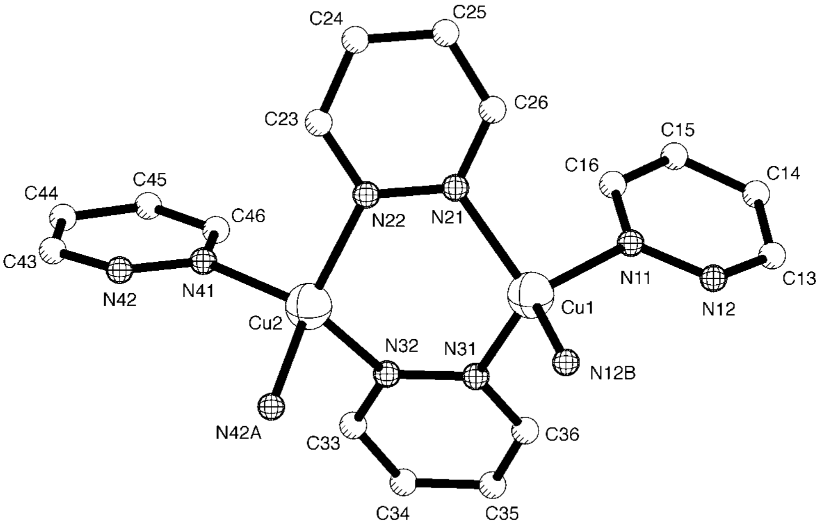


Figure 2. Presentation of the pseudo-tetrahedrally coordinated copper centres Cu1 and Cu2 by pyridazine with the numbering of the atoms.

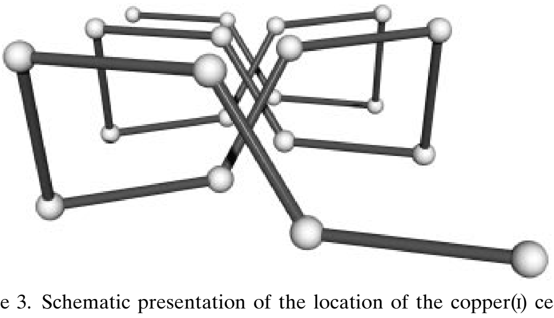


Figure 3. Schematic presentation of the location of the copper(I) centres (balls) of coordination polymer **4**. View along the crystallographic *c* axis. In order to clarify the *meso*-helical arrangement, the positions of the copper centres were scaled along *c* by a factor of 0.125.

ligands. The micro analytical data confirm as well the composition of **4**.

The formation of **4** becomes clear, if one assumes initial reaction of dication $[Cu_2(H_3CCN)_2(\mu\text{-pydz})_3]^{2+}$ ($\mathbf{1}^{2+}$) with two molecules of bidentate phosphane $CH_2(CH_2PPh_2)_2$ (**2**) to form mononuclear complex $[Cu\{CH_2(CH_2PPh_2)_2\}_2]^+$ ($\mathbf{3}^+$) and ionic mononuclear key intermediate $[Cu(pydz)_3(H_3CCN)]^+$ ($\mathbf{5}^+$) with elimination of one molecule of acetonitrile. Reaction of key intermediate $\mathbf{5}^+$ with $\mathbf{1}^{2+}$ and elimination of one molecule of acetonitrile yields the $[Cu_3(\mu\text{-pydz})_4(pydz)_2(H_3CCN)_2]^{3+}$ ($\mathbf{6}^{3+}$) ion. Elongation of $\mathbf{6}^{3+}$ by $\mathbf{5}^+$ and loss of two molecules of acetonitrile affords $[Cu_4(\mu\text{-pydz})_6(pydz)_3(H_3CCN)]^{4+}$ ($\mathbf{7}^{4+}$). Repetitive application of the elongation steps finally leads to the coordination polymer ${}^1_\infty\{[Cu(\mu\text{-pydz})_2][PF_6]\}$ (**4**) (Scheme 2).

The reaction mechanism given for the formation of coordination polymer **4** is supported by further experimental material. As the ratio Cu/pyridazine is 1:1.5 in the starting material **1** and 1:2 in the product **4**, one would expect that the reaction of **1** plus pyridazine without phosphane **2** should also generate **4**. However, instead of **4**, the dinuclear species $[Cu_2(\mu\text{-pydz})_3(pydz)_2][PF_6]_2$ was isolated.[18] A second route to raise the Cu/pyridazine ratio from 1:1.5 of **1** to 1:2 for product **4** is extrusion of copper from **1** with

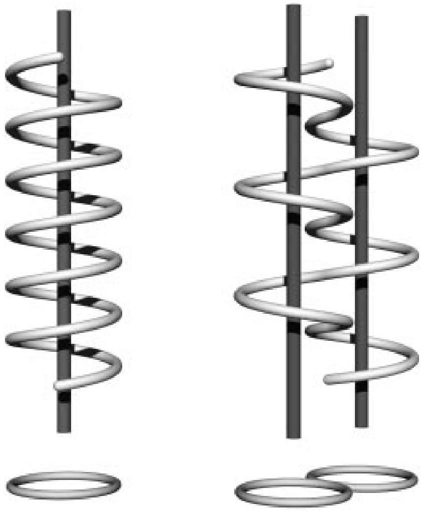
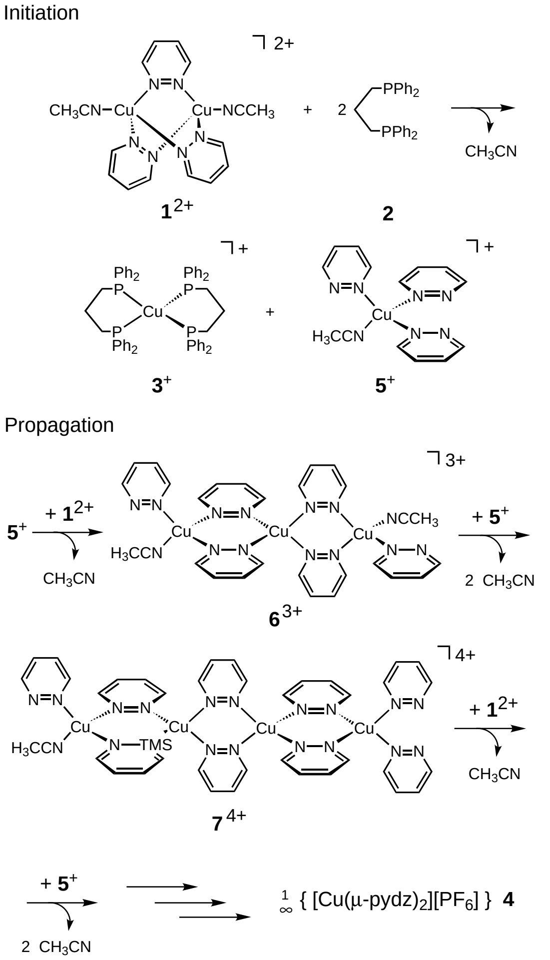


Figure 4. Generation of a helix and a *meso*-helix from a circle and a lemniscate.



Scheme 2. Proposed mechanism for the formation of **4**. For stereochemical details of **4** see details of X-ray structure analysis and Figure 1.

1,3-bis(diphenylphosphanyl)propane (**2**). This hypothesis is confirmed by the fact, that coordination polymer **4** was formed almost quantitatively from a 1:1 mixture of **1** and **2** together with mononuclear phosphanecopper(I) complex $[Cu\{CH_2(CH_2PPh_2)_2\}_2][PF_6]$ (**3**).[14]

Experimental Section

General: All manipulations were performed under dry dinitrogen with standard Schlenk techniques. Solvents were dried and distilled before use. 1,3-Bis(diphenylphosphanyl)propane and pyridazine were purchased from Acros Organics and used without further purification. IR spectra were recorded on a Bruker IFS25 spectrophotometer as KBr pellets. NMR spectra were recorded with a JEOL JNM-GX-400 spectrometer. Mass spectra were recorded on a micromass ZabSpec (ion-desorption from a *m*-nitrobenzyl alcohol matrix: 8 KeV, caesium atoms FAB-MS). Elemental analyses were performed in the microanalytical laboratory of the Institut für Organische Chemie, Universität Erlangen-Nürnberg by standard procedures. $[Cu_2(H_3CCN)_2(\mu\text{-pydz})_3][PF_6]_2$ (**1**) was obtained on addition of $[Cu(H_3CCN)_4][PF_6]$ to an equimolar amount of pyridazine dissolved in acetonitrile.[15]

$^1_\infty\{[Cu(\mu\text{-pydz})_2][PF_6]\}$ (4): Compound **2** (0.202 g, 0.49 mmol) was added to a solution of **1** (0.365 g, 0.49 mmol) in acetonitrile (30 mL) at 20 °C and the resulting pale yellow solution was stirred at 20 °C for 18 h. The solvent was removed in vacuo and the remaining residue was dissolved in a minimum of dichloromethane and filtered. Addition of hexane to this solution led to the formation of a yellow precipitate. The supernatant solution was extracted by using a cannula and the precipitate was washed several times with small volumes of hexane. After crystallisation from dichloromethane/hexane (1:1) at 20 °C, compound **4** was obtained as yellow-orange crystals, suitable for X-ray diffraction studies. IR (KBr): $\tilde{\nu} = 3056$ (w), 1633 (w), 1571 (m), 1440 (s), 1426 (w), 1418 (s), 830 (vs), 762 (s), 673 (w), 560 cm^{-1} (s); ^1H NMR (400 MHz, CD_3CN, 25 °C, TMS): $\delta = 9.28$ (br, 2H), 7.81 (br, 2H); elemental analysis calcd(%) for $C_8H_8N_4PF_6Cu$ (369.69): C 26.06, H 2.19, N 15.20; found: C 26.02, H 2.23, N 15.28.

$[Cu\{CH_2(CH_2PPh_2)_2\}_2][PF_6]$ (3): The remaining supernatant solution of the preparation of **4** was evaporated in vacuo and the remaining viscous residue was crystallised from acetonitrile/acetone (1:1). IR (KBr): $\tilde{\nu} = 3054$ (m), 2926 (m), 1483 (m), 1435 (s), 840 (vs), 742 (s), 696 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.40-7.10$ (br, 20H), 2.30 (br, 4H), 1.65 (br, 2H); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -9.49$; MS(FAB): m/z (%): 887 (58) $[M - PF_6]^+$, 475 (100) $[M - PF_6 - Ph_2P(CH_2)_3PPh_2]^+$.[14]

X-ray structure determination of 4: A crystal with dimensions 0.40 × 0.30 × 0.20 mm was mounted in a glass capillary and investigated with a Nonius Kappa CCD-MACH3 diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation by use θ and ω scans. The structure was solved by direct methods (SHELX-97)[19] and refined by full-matrix least-squares treatment against F^2 with the SHELXL-97 program system.[20] All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed in ideal positions (riding model) and were included without refinement and with fixed isotropic *U*.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158438. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] A. E. Rowan, R. J. M. Nolte, *Angew. Chem.* **1998**, *110*, 65-71; *Angew. Chem. Int. Ed.* **1998**, *37*, 63-68; J.-M. Lehn, *Angew. Chem.* **1990**, *102*, 1347-1362; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304-1319; D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725-2828.

[2] D. J. Williams, H. M. Colquhoun, C. A. O'Mahoney, *J. Chem. Soc. Chem. Commun.* **1994**, 1643-1644.

[3] G. S. Hanan, J.-M. Lehn, N. Kyritsakas, J. Fischer, *J. Chem. Soc. Chem. Commun.* **1995**, 765-766; D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Angew. Chem.* **1997**, *109*, 1931-1933; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1845-1846.

[4] R. J. M. Nolte, *Chem. Soc. Rev.* **1994**, 11-19.

[5] K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584-587; *Angew. Chem. Int. Ed.* **1999**, *38*, 492-495.

[6] T. Ezuhara, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 3279-3283.

[7] See also: a) H. Koshima, E. Hayashi, T. Matsuura, K. Tanaka, F. Toda, M. Kato, M. Kiguchi, *Tetrahedron Lett.* **1997**, *38*, 5009-5012; b) D. K. Kondepudi, R. J. Kaufmann, N. Singh, *J. Am. Chem. Soc.* **1993**, *115*, 10211—10216.

[8] R. F. Carina, G. Bernardinelli, A. F. Williams, *Angew. Chem.* **1993**, *105*, 1483-1485; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1463-1465; O. J. Gelling, F. van Bolhuis, B. L. Feringa, *J. Chem. Soc. Chem. Commun.* **1991**, 917-919; C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White , *Angew. Chem.* **1998**, *110*, 970-973; *Angew. Chem. Int. Ed.* **1998**, *37*, 920-922; L. Carlucci, G. Ciani, D. W. V. Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, *36*, 3812-3813.

[9] R. W. Saalfrank, M. Decker, F. Hampel, K. Peters, H. G. von Schnering, *Chem. Ber./Recl.* **1997**, *130*, 1309-1313; D. A. Evans, K. A. Woerpel, M. J. Scott, *Angew. Chem.* **1992**, *104*, 439-441; *Angew.*

Chem. Int. Ed. Engl. **1992**, *31*, 430–433; J. F. Modder, G. van Koten, K. Vrieze, A. L. Spek, *Angew. Chem.* **1989**, *101*, 1723–1725; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1698–1700; P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis, S. B. Wild, *Chem. Commun.* **1998**, 1153–1154; B. Wu, W.-J. Zhang, S.-Y. Yu, X.-T. Wu, *J. Chem. Soc. Dalton Trans.* **1997**, 1795–1796.

[10] M. Kimura, M. Sano, T. Muto, K. Hanabusa, H. Shirai, N. Kobayashi, *Macromolecules* **1999**, *32*, 7951–7953.

[11] R. W. Saalfrank, H. Maid, F. Hampel, K. Peters, *Eur. J. Inorg. Chem.* **1999**, 1859–1867; R. W. Saalfrank, O. Struck, K. Peters, H. G. von Schnering, *Inorg. Chim. Acta* **1994**, *222*, 5–11.

[12] P. Luger, *Angew. Chem.* **1998**, *110*, 3548–3551; *Angew. Chem. Int. Ed.* **1998**, *37*, 3353–3357.

[13] G. Becker, B. Eschbach, O. Mundt, N. Seidler, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1381–1390; R. A. Bartlett, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1986**, *25*, 1243–1247.

[14] P. Comba, C. Katsichtis, B. Nuber, H. Pritzkow, *Eur. J. Inorg. Chem.* **1999**, 777–783.

[15] M. Maekawa, M. Munakata, T. Kudowa-Sowa, Y. Nozaka, J. *Chem. Soc. Dalton Trans.* **1994**, 603–607.

[16] N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia, G. La Monica, *J. Am. Chem. Soc.* **1994**, *116*, 7668–7676; G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi, A. Maspero, M. Moret, *Inorg. Chem.* **1998**, *37*, 4284–4292.

[17] D. T. Cromer, A. C. Larson, *Acta Crystallogr Sect. B* **1972**, *28*, 1052–1058; T. Fetzer, A. Lentz, T. Debaerdemaeker, *Z. Naturforsch. Teil B* **1990**, *45*, 199–202; T. Kromp, W. S. Sheldrick, *Z. Naturforsch. Teil B* **1999**, *54*, 1175–1180; L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Inorg. Chem.* **1998**, *37*, 5941–5943.

[18] According to an X-ray structure analysis, the two copper(I) ions in $[Cu_2(\mu\text{-pydz})_3(\text{pydz})_2][PF_6]_2$ bind three bridging and one terminal pyridazine ligands, each. Triclinic, space group $P\bar{1}$, $a = 11.574(2)$, $b = 12.431(2)$, $c = 13.015\ (2)$ Å, $\alpha = 65.37(10)$, $\beta = 71.24(10)$, $\gamma = 70.69(10)°$.

[19] G. M. Sheldrick, SHELX-97, Program for the Solution of Crystal Structures, Universität Göttingen (Germany), **1997**.

[20] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen (Germany), **1997**.

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