

Self-assembly of 1D- and 3D-Networks Through Non-coordination Intermolecular Forces: Synthesis and Crystal Structures of Copper(I) Complexes Based on Pyridazine-type Ligands

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Dedicated to Professor Dr. Rolf W. Saalfrank

Reaction of $[\text{Cu}_2(\text{H}_3\text{CCN})_2(\mu\text{-pydz})_3][\text{PF}_6]_2$ (**1**) with an excess of pyridazine or phthalazine yielded the novel dinuclear complexes $[\text{Cu}_2(\mu\text{-pydz})_3(\text{pydz})_2][\text{PF}_6]_2$ (**2**) and $[\text{Cu}_2(\mu\text{-pydz})(\mu\text{-phtz})_2(\text{phtz})_2][\text{PF}_6]_2$ (**5**), respectively. Depolymerisation of the coordination polymer $\infty\{[\text{Cu}(\mu\text{-pydz})_2][\text{PF}_6]\}$ (**3**) in dichloromethane by addition of an excess of benzo[c]cinnoline afforded the dinuclear copper(I) salt $[\text{Cu}_2(\mu\text{-pydz})_2(\text{pydz})_2(\text{benzo}[\text{c}]\text{cinnoline})_2][\text{PF}_6]_2$ (**4**). Furthermore, a new route for the preparation of bis(benzonitrile)tris(μ -phthalazine)dicopper(I) bis(trifluoromethanesulfonate), $[\text{Cu}_2(\text{C}_6\text{H}_5\text{CN})_2(\mu\text{-phtz})_3][\text{CF}_3\text{SO}_3]_2$ (**7**), was established from $\{[\text{Cu}(\text{CF}_3\text{SO}_3)]_2 \cdot \text{C}_6\text{H}_5\text{Me}\}$, phthalazine and benzonitrile *via* the very air-sensitive intermediate $[\text{Cu}_2(\text{CF}_3\text{SO}_3)_2(\mu\text{-phtz})_3]$ (**6**). Copper(I) compounds **2**, **4**, and **7** were completely characterised and the molecular structures confirmed in the solid state by single-crystal X-ray structure determination. The analysis of the packing of the molecules in crystals of **4** and **7** revealed a self-assembly of one- and three-dimensional frameworks, respectively, resulting from intermolecular π - π stacking interactions between pyridazine-type ligands.

Key words: Copper(I), Pyridazine, Phthalazine, Benzo[c]cinnoline, Self-assembly

Introduction

In the past we reported on the synthesis and the crystal structure of an unexpected *meso*-helical coordination polymer $\infty\{[\text{Cu}(\mu\text{-pydz})_2][\text{PF}_6]\}$ (**3**), together with the mononuclear copper(I) complex $[\text{Cu}(\text{dppp})_2][\text{PF}_6]$, from the reaction of achiral dinuclear $[\text{Cu}_2(\text{H}_3\text{CCN})_2(\mu\text{-pydz})_3][\text{PF}_6]_2$ (**1**) (pydz = pyridazine) with the bidendate 1,3-bis(diphenylphosphanyl)propane (dppp) [1]. The resulting coordination polymer **3** consisted of a one-dimensional infinite chain exclusively composed of copper(I) ions bridged by achiral pyridazine ligands. The detailed analysis of the one-dimensional infinite framework of **3** revealed that eight copper centres constitute the repeating unit, creating a non-common *meso*-helix. The reaction mechanism proposed for the formation of coordination polymer **3** was supported experimentally. In the course of our ongoing studies on coordination polymers [2], the reactions of **1** as a starting material with an ex-

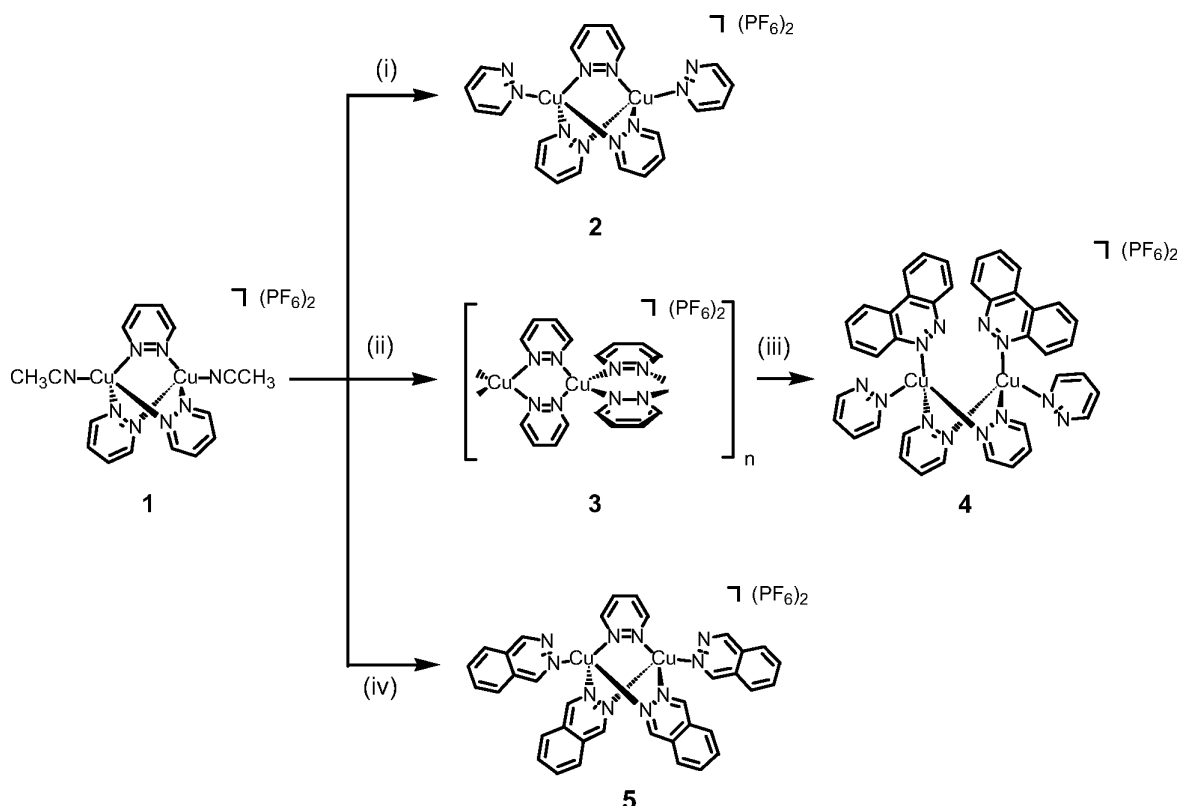
cess of pyridazine, benzo[c]cinnoline (*via* coordination polymer **3**), or phthalazine (phtz) were investigated, which yielded the new dinuclear complexes $[\text{Cu}_2(\mu\text{-pydz})_3(\text{pydz})_2][\text{PF}_6]_2$ (**2**), $[\text{Cu}_2(\mu\text{-pydz})_2(\text{pydz})_2(\text{benzo}[\text{c}]\text{cinnoline})_2][\text{PF}_6]_2$ (**4**), and $[\text{Cu}_2(\mu\text{-pydz})(\mu\text{-phtz})_2(\text{phtz})_2][\text{PF}_6]_2$ (**5**), respectively. In addition, the synthesis and characterisation of complexes $[\text{Cu}_2(\text{CF}_3\text{SO}_3)_2(\mu\text{-phtz})_3]$ (**6**) and $[\text{Cu}_2(\text{C}_6\text{H}_5\text{CN})_2(\mu\text{-phtz})_3][\text{CF}_3\text{SO}_3]_2$ (**7**) are discussed in detail in this contribution.

Results and Discussion

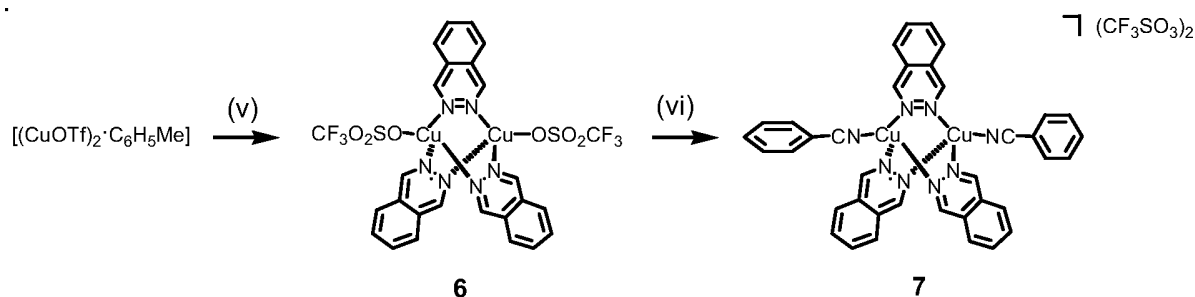
Synthetic pathways of compounds **2–7** are summarised in Schemes 1 and 2.

*Exposure of $[\text{Cu}_2(\text{H}_3\text{CCN})_2(\mu\text{-pydz})_3][\text{PF}_6]_2$ (**1**) to pyridazine and phthalazine*

The reaction of $[\text{Cu}(\text{H}_3\text{CCN})_4][\text{PF}_6]$ with pyridazine in acetonitrile leads to the formation of the



Scheme 1. Reagents and conditions: (i) pydz, CH₃CN, room temperature (r. t.), 12 h, crystallisation from CH₂Cl₂/*n*-hexane; (ii) dppp, r. t., 18 h, CH₃CN, crystallisation from CH₂Cl₂/*n*-hexane [1]; (iii) benzo[c]cinnoline, CH₂Cl₂, r. t., 48 h, crystallisation from CH₂Cl₂/*n*-hexane; (iv) phtz, CH₃CN, r. t., 12 h, crystallisation from CH₂Cl₂/*n*-hexane.



Scheme 2. Reagents and conditions: (v) phtz, CH₂Cl₂, r. t., 2 h, crystallisation from CH₂Cl₂/*n*-hexane; (vi) benzonitrile, 72 h, r. t., crystallisation from benzonitrile/*n*-hexane.

known dinuclear copper(I) complex cation present in **1**. The molecular structure of the cation of **1** consists of two tetrahedral copper(I) centres bridged by three pyridazine molecules and terminally coordinated acetonitrile ligands [3]. In the presence of an excess of pyridazine, the labile axial acetonitrile ligands are replaced by two supplementary pyridazine molecules yielding the novel dinuclear copper(I) salt [Cu₂(μ-

pydz)₃(pydz)₂][PF₆]₂ (**2**) [4]. Air-sensitive single crystals of **2**, suitable for an X-ray structure determination, were grown from a mixture of dichloromethane/*n*-hexane [crystal system: triclinic; space group: *P* $\bar{1}$; *a* = 11.5747(2), *b* = 12.4317(2), *c* = 13.0158(2) Å, α = 65.379(1), β = 71.249(1), γ = 70.694(1)°, *V* = 1569.59(4) Å³]. The molecular structure of **2** is analogous to that of the dinuclear silver salt [Ag₂(μ-

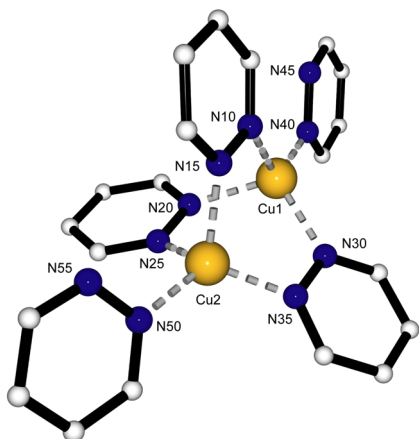


Fig. 1. Molecular structure of the dication of compound **2** [POVRAY presentation, hydrogen atoms and hexafluorophosphate counter anions (PF_6^-) omitted for clarity; Cu grey, N dark, C white; colour version: Cu gold, N blue, C white (online)]. Selected bond lengths (\AA) and angles (deg): Cu(1)–Cu(2) 3.069(3), Cu(1)–N(40) 2.009(3), Cu(2)–N(50) 2.006(3), Cu(1)–N(30) 2.030(3), Cu(1)–N(20) 2.074(3), Cu(1)–N(10) 2.058(3), Cu(2)–N(35) 2.011(3), Cu(2)–N(25) 2.077(3), Cu(2)–N(15) 2.063(3), N(10)–N(15) 1.348(3); N(40)–Cu(1)–N(30) 118.85(10), N(40)–Cu(1)–N(10) 116.71(11), N(30)–Cu(1)–N(10) 107.66(10), N(40)–Cu(1)–N(20) 107.64(11), N(30)–Cu(1)–N(20) 108.05(11), N(10)–Cu(1)–N(20) 95.00(11).

$\text{pydz})_3(\text{pydz})_2][\text{CF}_3\text{SO}_3]_2$ reported by G. Ciani and co-workers [5]. In **2**, both copper(I) ions are triply bridged by three pyridazine ligands [$\text{Cu}–\text{N}_{(\mu-\text{pydz})} = 2.05 \text{ \AA}$ (mean)], and the coordination sphere of each metal centre is complemented by one η^1 pyridazine molecule [$\text{Cu}–\text{N}_{(\text{terminal pydz})} = 2.00 \text{ \AA}$ (mean)]. The molecular structure of **2** is depicted in Fig. 1 with a partial labeling of atoms.

When complex **1** is exposed to an excess of phthalazine, substitution of the terminal acetonitrile and two bridging pyridazine ligands by four phthalazine molecules is observed, affording the dinuclear copper(I) salt $[\text{Cu}_2(\mu-\text{pydz})(\mu-\text{phtz})_2(\text{phtz})_2][\text{PF}_6]_2$ (**5**). Orange-red crystals of **5** were obtained by vapour diffusion of *n*-hexane into the dichloromethane mother liquor, but the data set is presently not satisfactory for publication. Nevertheless, the stoichiometry of a structure **5**, consisting of two copper(I) centres terminally coordinated by two phthalazine molecules and bridged by two phthalazine and one pyridazine ligands, has been confirmed by elemental analysis $[\text{C}_{36}\text{H}_{28}\text{Cu}_2\text{F}_{12}\text{N}_{10}\text{P}_2 (1017.71): \text{calcd. C } 42.49, \text{H } 2.77, \text{N } 13.76; \text{found C } 42.75, \text{H } 2.59, \text{N } 13.48.]$.

Reaction of the coordination polymer

$^1_2[\text{Cu}(\mu-\text{pydz})_2][\text{PF}_6]\} (\mathbf{3})$ with benzo[*c*]cinnoline

In a previous publication we reported that reaction of **1** with bidentate 1,3-bis(diphenylphosphanyl)propane yields the mononuclear copper(I) complex $[\text{Cu}(\text{dppp})_2][\text{PF}_6]$ [6] together with the one-dimensional coordination polymer **3** [1]. If the polymer **3** is subsequently reacted with an excess of benzo[*c*]cinnoline in dichloromethane, depolymerisation is observed affording the unexpected dinuclear copper(I) salt $[\text{Cu}_2(\mu-\text{pydz})_2(\text{pydz})_2(\text{benzo}[c]\text{cinnoline})_2][\text{PF}_6]_2$ (**4**). Crystallisation of **4** by vapour diffusion of *n*-hexane into the dichloromethane mother liquor afforded single crystals suitable for X-ray diffraction. Complex **4** crystallises in the monoclinic space group $P2_1/c$ with $a = b = 16.177(3)$, $c = 16.391(3) \text{ \AA}$, $\beta = 91.43(3)^\circ$, and $V = 4288.1(15) \text{ \AA}^3$. The two copper(I) atoms of the dication of **4** have a *pseudo*-tetrahedral coordination geometry arising from two bridging pyridazine [$\text{Cu}–\text{N}_{(\mu-\text{pydz})} = 2.05 \text{ \AA}$ (mean)], one terminal η^1 pyridazine [$\text{Cu}–\text{N}_{(\text{terminal pydz})} = 2.06 \text{ \AA}$ (mean)], and one terminal η^1 benzo[*c*]cinnoline ligands [$\text{Cu}–\text{N}_{(\text{benzo}[c]\text{cinnoline})} = 2.03 \text{ \AA}$ (mean)]. Until now several modes of coordination of benzo[*c*]cinnoline ligands have been described in the literature [7–11]. The rare η^1 coordination mode was already observed in the structure of (benzo[*c*]cinnoline)pentacarbonyltungsten ($\text{W}–\text{N} = 2.28 \text{ \AA}$) [12]. A POVRAY presentation of the molecular structure of **4**, together with selected bond lengths and angles, is given in Fig. 2. In complex **4** both benzo[*c*]cinnoline molecules adopt an η^1 coordination mode and present the particularity to be oriented in parallel but opposite direction. This unusual arrangement of benzo[*c*]cinnoline ligands in **4** allows *intra*- as well as *intermolecular* $\pi-\pi$ interactions. The *intra*- and *intermolecular* separations of parallel benzo[*c*]cinnoline ligands are 3.35 and 3.49 \AA , respectively. For such face-to-face $\pi-\pi$ interactions, the distance between the arene planes is commonly around 3.3 to 3.8 \AA [13]. In addition, the intermolecular $\pi-\pi$ interactions of **4** induce the self-assembly of a one-dimensional chain (see Fig. 3). Arene-arene interactions in metal complexes with aromatic nitrogen-containing ligands were previously documented by C. Janiak [14], and several structures of multidimensional supramolecular networks based on such weak interactions have been published [2a, 15]. Compound **4** constitutes an additional example of the fascinat-

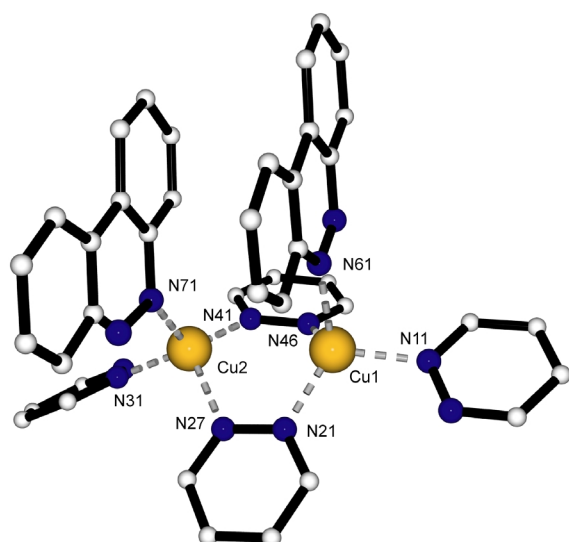


Fig. 2. Molecular structure of the dication of compound **4** [POVray presentation, hydrogen atoms and hexafluorophosphate counter anions (PF_6^-) omitted for clarity; Cu grey, N dark, C white; colour version: Cu gold, N blue, C white (online)]. Selected bond lengths (Å) and angles (deg): Cu(1)–Cu(2) 3.231(4), Cu(1)–N(11) 2.048(4), Cu(2)–N(31) 2.069(4), Cu(1)–N(61) 2.043(4), Cu(2)–N(71) 2.021(4), Cu(1)–N(46) 2.078(4), Cu(1)–N(21) 2.005(4), Cu(2)–N(41) 2.012(4), Cu(2)–N(27) 2.089(4); N(21)–Cu(1)–N(61) 123.51(16), N(21)–Cu(1)–N(11) 112.12(15), N(61)–Cu(1)–N(11) 101.12(16), N(21)–Cu(1)–N(46) 108.14(16), N(61)–Cu(1)–N(46) 99.03(15), N(11)–Cu(1)–N(46) 112.20(16).

ing self-assembly generated by parallel arene-arene π stacking interactions.

Reaction of $\{[\text{Cu}(\text{CF}_3\text{SO}_3)]_2 \cdot \text{C}_6\text{H}_5\text{Me}\}$ with phthalazine in benzonitrile

P. Hubberstey and co-workers have reported on the molecular structure of a tris(pyridazine)-bridged dinuclear cation with terminal benzonitrile ligands generated in the reaction of $[\text{Cu}(\text{H}_3\text{CCN})_4][\text{BF}_4]$ with pyridazine in benzonitrile [3]. We now present a new route for the synthesis of this type of complexes and we describe in particular the preparation and the structural characterisation of the original phthalazine analogue $[\text{Cu}_2(\text{C}_6\text{H}_5\text{CN})_2(\mu\text{-phtz})_3][\text{PF}_6]_2$ (**7**) obtained from $\{[\text{Cu}(\text{CF}_3\text{SO}_3)]_2 \cdot \text{C}_6\text{H}_5\text{Me}\}$, phthalazine and benzonitrile *via* the very air-sensitive intermediate $[\text{Cu}_2(\text{CF}_3\text{SO}_3)_2(\mu\text{-phtz})_3]$ (**6**) (Scheme 2). In the first step, reaction of $\{[\text{Cu}(\text{CF}_3\text{SO}_3)]_2 \cdot \text{C}_6\text{H}_5\text{Me}\}$ with phthalazine in dichloromethane at r. t. led to the formation of complex **6**. All our efforts to grow single crystals for X-ray diffraction analysis remained

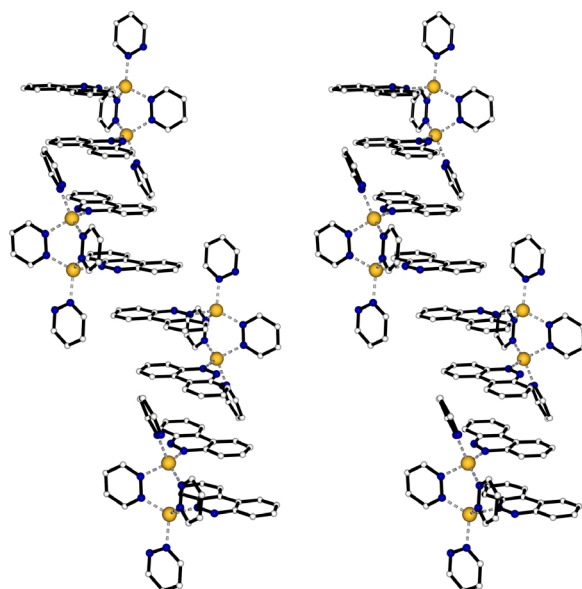


Fig. 3. Stereoview (POVray presentation) of the 1D-ordination chain built up by the cations of **4** [counter ions, disorder and hydrogen atoms omitted for clarity; Cu grey, N dark, C white; colour version: Cu gold, N blue, C white (online)]. The strands, self-assembled *via* π - π interactions, run along the *a* axis of the unit cell.

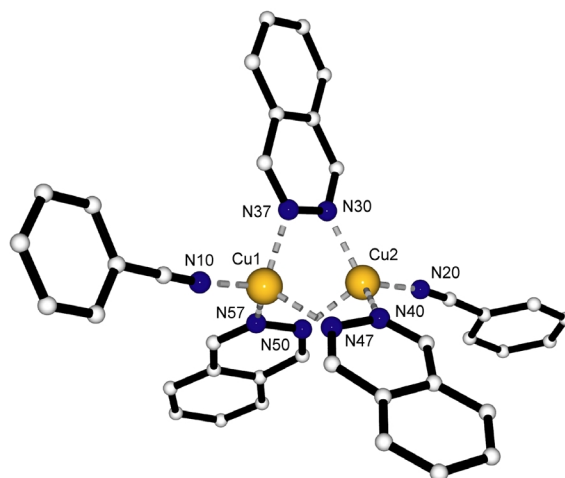


Fig. 4. Molecular structure of the dication of compound **7** [POVray presentation, hydrogen atoms and counter anions (CF_3SO_3^-) omitted for clarity; Cu grey, N dark, C white; colour version: Cu gold, N blue, C white (online)]. Selected bond lengths (Å) and angles (deg): Cu(1)–Cu(2) 3.050(3), Cu(1)–N(10) 1.917(3), Cu(1)–N(57) 2.030(4), Cu(1)–N(47) 2.044(4), Cu(1)–N(37) 2.051(3), Cu(2)–N(20) 1.940(3), Cu(2)–N(30) 2.042(3), Cu(2)–N(40) 2.078(3), Cu(2)–N(50) 2.086(3); N(10)–Cu(1)–N(57) 119.08(12), N(10)–Cu(1)–N(47) 112.59(12), N(57)–Cu(1)–N(47) 102.63(11), N(10)–Cu(1)–N(37) 110.58(12), N(57)–Cu(1)–N(37) 102.60(11), N(47)–Cu(1)–N(37) 108.42(11).

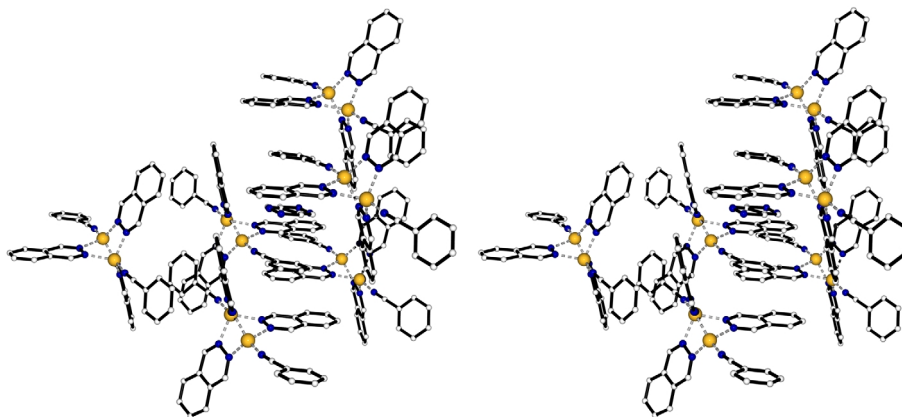


Fig. 5. Stereoview (POVRAY presentation) of the 3D-network built up by the cations of compound **7** [counter ions, disorder (except for free phthalazine ligand) and hydrogen atoms omitted for clarity; Cu grey, N dark, C white; colour version: Cu gold, N blue, C white (online)]. The 1D-chain is based on π - π interactions between ligands of four dicopper(I) complexes and a free phthalazine ligand (in direction of the *b* axis). Extension to a 2D-sheet structure is visualised by the π - π interaction of two phthalazine ligands (background). The 3D-network results from further π stacking of two benzonitrile ligands (left side).

unsuccessful, but elemental analysis data are in good agreement with the composition specified above [$\text{C}_{26}\text{H}_{18}\text{Cu}_2\text{F}_{12}\text{N}_6\text{O}_6\text{S}_2$ (815.67): calcd. C 38.28, H 2.22, N 10.30; found C 38.18, H 2.37, N 10.17]. When **6** was dissolved in benzonitrile, both terminal trifluoromethanesulfonate ligands were replaced by two benzonitrile molecules giving the dinuclear bis(benzonitrile)tris(μ -phthalazine)dicopper(I) complex [$\text{Cu}_2(\text{C}_6\text{H}_5\text{CN})_2(\mu\text{-phtz})_3][\text{CF}_3\text{SO}_3]_2$ (**7**). Single crystals of **7**, suitable for an X-ray structure determination were grown by vapour phase diffusion of *n*-hexane into the benzonitrile mother liquor [crystal system: triclinic; space group: $P\bar{1}$; $a = 9.8197(2)$, $b = 13.6924(3)$, $c = 17.9239(4)$ Å, $\alpha = 108.353(1)$, $\beta = 96.115(1)$, $\gamma = 97.173(1)^\circ$, $V = 2242.09(8)$ Å³]. A POV-Ray view of the structure and selected bond lengths and angles are presented in Fig. 4. The molecular structure of the dinuclear cation of **7** consists of two *pseudo*-tetrahedral copper(I) centres bridged by three phthalazine molecules [$\text{Cu}-\text{N}_{(\mu\text{-phtz})} = 2.05$ Å (mean)]. The coordination of each copper(I) centre is completed by one terminally bound benzonitrile ligand [$\text{Cu}-\text{N}_{(\text{benzonitrile})} = 1.93$ Å (mean)]. The phthalazine-based framework is comparable to that of the pyridazine analogue reported by P. Hubberstey *et al.* [$\text{Cu}-\text{N}_{(\mu\text{-pydz})} = 2.05$ Å (mean), $\text{Cu}-\text{N}_{(\text{benzonitrile})} = 1.93$ Å (mean)].

The unique structure of compound **7** arises from the self-assembly of the dinuclear units by weak intermolecular interactions giving rise to a remarkable

three-dimensional organisation as depicted in Fig. 5. As in the case of complex **4**, the observed supramolecular network results only from arene-arene π stacking bringing into play successively a phthalazine ligand, a benzonitrile ligand, a disordered free phthalazine, a benzonitrile ligand, and a phthalazine ligand of four different dinuclear complexes. This sequence can be considered as the “repeating unit” of the one-dimensional network. The free phthalazine molecules integrated in the crystal lattice were probably produced in the synthesis of the air-sensitive complex **6**. As further shown in Fig. 5, the expansion of the structure to a two-dimensional and finally to a three-dimensional array is ensured by weak π - π interaction of phthalazine and benzonitrile ligands, respectively (background and left side of the stereo presentation in Fig. 5) [15]. The distances between the arenes of compound **7** range from 3.45 to 3.59 Å [13, 14].

Experimental Section

General procedures and materials

All manipulations were performed under dry dinitrogen using standard Schlenk techniques. Solvents were dried according to standard procedures and distilled before use. Pyridazine, phthalazine and benzo[*c*]cinnoline were purchased from Acros Organics and used without further purification. IR spectra were recorded on a Bruker IFS 25 spectrophotometer for KBr pellets. NMR spec-

Table 1. Crystal and structure refinement data for **2**, **4**, and **7**.

	2	4	7
Molecular formula	C _{20.50} H ₂₁ ClCu ₂ F ₁₂ N ₁₀ P ₂	C ₄₀ H ₃₂ Cu ₂ F ₁₂ N ₁₂ P ₂	C ₄₃ H ₃₁ Cu ₂ F ₆ N ₉ O ₆ S ₂
<i>M_r</i> , g mol ^{−1}	859.93	1097.80	1074.97
Crystal colour	orange	red	yellow
Crystal size, mm ³	0.35 × 0.35 × 0.30	0.30 × 0.30 × 0.30	0.30 × 0.20 × 0.20
Crystal system	triclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.5747(2)	16.177(3)	9.8197(2)
<i>b</i> , Å	12.4317(2)	16.177(3)	13.6924(3)
<i>c</i> , Å	13.0158(2)	16.391(3)	17.9239(4)
α , deg	65.379(1)	90	108.353(1)
β , deg	71.249(1)	91.43(3)	96.115(1)
γ , deg	70.694(1)	90	97.173(1)
<i>V</i> , Å ³	1569.59(4)	4288.1(15)	2242.09(8)
<i>Z</i>	2	4	2
<i>T</i> , K	173(2)	173(2)	173(2)
ρ_{calc} , g cm ^{−3}	1.82	1.70	1.59
Absorption coeff., mm ^{−1}	1.6	1.2	1.1
<i>F</i> (000), e	852	2208	1088
θ Range, °	1.76 to 27.53	1.26 to 27.49	1.21 to 25.01
<i>hkl</i> Range	−15 ≤ <i>h</i> ≤ 15, −16 ≤ <i>k</i> ≤ 16, −16 ≤ <i>l</i> ≤ 16	−20 ≤ <i>h</i> ≤ 21, −17 ≤ <i>k</i> ≤ 21, −21 ≤ <i>l</i> ≤ 21	−11 ≤ <i>h</i> ≤ 11, −16 ≤ <i>k</i> ≤ 16 −21 ≤ <i>l</i> ≤ 21
Reflections collected	13306	16271	14990
Independent reflections	7138	9763	7865
<i>R</i> _{int}	0.017	0.029	0.025
Max./min. transm.	0.6380/0.5965	0.7209/0.7209	0.8062/0.7288
Data/parameters	7138/433	9763/603	7865/622
Goodness-of-fit on <i>F</i> ²	1.028	1.372	1.050
Final <i>R</i> 1 indices [<i>I</i> ≥ 2σ(<i>I</i>)]	0.049	0.069	0.046
<i>wR</i> 2 (all data)	0.147	0.218	0.141
Largest diff. peak/hole, e Å ^{−3}	1.15/−1.04	1.56/−1.21	0.91/−0.50

tra were recorded with a JEOL JNM-GX-400 spectrometer at 400 MHz for ¹H (25 °C) for diluted CD₃CN solutions using Me₄Si as an internal standard; δ values are given in ppm. The resonance multiplicity is indicated as s (singlet) and m (multiplet). Mass spectra were recorded on a micromass ZabSpec instrument (ion-desorption from a *m*-nitrobenzyl alcohol matrix: 8 KeV, caesium FAB-MS). Elemental analyses were performed in the microanalytical laboratory of the Institut für Organische Chemie, Universität Erlangen-Nürnberg on a EA 1110 CHNS-Microautomat by standard procedures. The copper(I) starting material, [Cu₂(H₃CCN)₂(μ-pydz)₃][PF₆]₂ (**1**) was obtained by addition of [Cu(H₃CCN)₄][PF₆] to an equimolar amount of pyridazine dissolved in acetonitrile [16], whereas {[Cu(CF₃SO₃)₂ · C₆H₅Me]} was prepared from the reaction of trifluoromethanesulfonic acid anhydride with copper(I) oxide in toluene [17].

Preparations

[Cu₂(μ-pydz)₃(pydz)₂][PF₆]₂ (**2**)

To a yellow solution of **1** (0.290 g, 0.39 mmol) in 20 mL of acetonitrile was added at 20 °C an excess of pyridazine

(0.157 g, 1.96 mmol), and the resulting orange solution was stirred at 20 °C. After 12 h the solvent volume was reduced (10 mL) under vacuum and addition of Et₂O (20 mL) led to the formation of an orange precipitate. The supernatant solution was taken off using a cannula and the precipitate was washed several times with small volumes of *n*-hexane. After crystallisation of the crude reaction product from dichloromethane/*n*-hexane (1 : 1) at 20 °C, compound **2** was obtained as orange crystals, suitable for X-ray diffraction studies. IR: ν = 1629m, 1571m, 1437m, 1419m, 1097s, 842vs, 759s, 559s cm^{−1}. – ¹H NMR: δ = 9.19 (br s, 10H, pydz), 7.66 (br s, 10H, pydz). – MS: *m/z* (%) = 143 (100) [Cu+pydz]⁺. – C₂₀H₂₀Cu₂F₁₂N₁₀P₂ (817.46): calcd. C 29.39, H 2.47, N 17.13; found C 29.69, H 2.49, N 17.07.

[Cu₂(μ-pydz)₂(pydz)₂(benzo[*c*]cinnoline)₂][PF₆]₂ (**4**)

To a suspension of $\frac{1}{\infty}$ {[Cu(μ-pydz)₂][PF₆]} (**3**) (0.200 g, 0.54 mmol of Cu^I) in 20 mL of CH₂Cl₂ was added at 20 °C an excess of benzo[*c*]cinnoline (0.150 g, 0.83 mmol), and the resulting clear red solution was stirred at 20 °C for 48 h. After filtration under nitrogen, red crystals of **4** suitable for X-ray diffraction studies were grown by the vapour phase diffusion

of *n*-hexane into the mother liquor. – IR: ν = 3082w, 1577m, 1451s, 1422m, 1409m, 1364w, 1126m, 1094m, 1066m, 844vs, 762s, 753s, 715m, 558 cm^{-1} . – ^1H NMR: δ = 9.18 (br s, 8H, pydz), 8.73–8.66 (m, 8H, benzo[c]cinnoline), 8.00–7.94 (m, 8H, benzo[c]cinnoline), 7.66 (br s, 8H, pydz). – MS: m/z (%) = 323 (40) $[\text{Cu}+\text{benzo}[\text{c}]\text{cinnoline}+\text{pydz}]^+$, 243 (28) $[\text{Cu}+\text{benzo}[\text{c}]\text{cinnoline}]^+$, 223 (28) $[\text{Cu}+(\text{pydz})_2]^+$, 181 (100) $[\text{benzo}[\text{c}]\text{cinnoline}+\text{H}]^+$. – $\text{C}_{40}\text{H}_{32}\text{Cu}_2\text{F}_{12}\text{N}_{12}\text{P}_2$ (1097.78): calcd. C 43.76, H 2.94, N 15.31; found C 43.41, H 2.94, N 15.11.

$[\text{Cu}_2(\mu\text{-pydz})(\mu\text{-phtz})_2(\text{phtz})_2][\text{PF}_6]_2$ (**5**)

Complex **5** was prepared in analogy to **2** using phthalazine (0.255 g, 1.96 mmol). The precipitate was redissolved in CH_2Cl_2 and orange-red crystals of **5** were grown by the vapour phase diffusion of *n*-hexane into the mother liquor. – IR: ν = 3059w, 1620m, 1577m, 1491m, 1447m, 1420w, 1380s, 1315w, 1277m, 1245w, 1161m, 842vs, 757s, 652m, 558s, 472s cm^{-1} . – ^1H NMR: δ = 10.12 (br s, 8H, phtz), 9.29 (br s, 2H, pydz), 8.30–8.11 (m, 16H, phtz), 7.75 (br s, 2H, pydz). – MS: m/z (%) = 405 (20) $[\text{Cu}+(\text{phtz})_2+\text{pydz}]^+$, 323 (100) $[\text{Cu}+(\text{phtz})_2]^+$, 273 (20) $[\text{Cu}+\text{phtz}+\text{pydz}]^+$, 193 (50) $[\text{Cu}+\text{phtz}]^+$. – $\text{C}_{36}\text{H}_{28}\text{Cu}_2\text{F}_{12}\text{N}_{10}\text{P}_2$ (1017.71): calcd. C 42.49, H 2.77, N 13.76; found C 42.75, H 2.59, N 13.48.

$[\text{Cu}_2(\text{CF}_3\text{SO}_3)_2(\mu\text{-phtz})_3]$ (**6**)

To a suspension of $\{[\text{Cu}(\text{CF}_3\text{SO}_3)]_2 \cdot \text{C}_6\text{H}_5\text{Me}\}$ (0.200 g, 0.66 mmol) in 20 mL of CH_2Cl_2 was added at 20 °C 0.085 g (0.66 mmol) of phthalazine, and the resulting clear yellow solution was stirred at 20 °C for 2 h. Addition of *n*-hexane led to the formation of a yellow precipitate. – $\text{C}_{26}\text{H}_{18}\text{Cu}_2\text{F}_6\text{N}_6\text{O}_6\text{S}_2$ (815.67): calcd. C 38.29, H 2.22, N 10.30; found C 38.18, H 2.37, N 10.17.

$[\text{Cu}_2(\text{C}_6\text{H}_5\text{CN})_2(\mu\text{-phtz})_3][\text{CF}_3\text{SO}_3]_2$ (**7**)

Compound **6** (0.200 g, 0.24 mmol) was dissolved in benzonitrile and the mixture was stirred for 72 h. Yellow crystals of **7**, suitable for X-ray diffraction analy-

sis, were grown by the vapour diffusion of *n*-hexane into the mother liquor. – IR: ν = 2229w, 1637m, 1629m, 1491w, 1447w, 1380m, 1261vs, 1168s, 1031s, 757s, 639s, 518w, 474m cm^{-1} . – ^1H NMR: δ = 9.73 (br s, 6H, phtz), 8.17–8.06 (m, 12H, phtz), 7.72–7.49 (m, 10H, benzonitrile). – MS: m/z (%) = 323 (100) $[\text{Cu}+(\text{phtz})_2]^+$, 193 (50) $[\text{Cu}+\text{phtz}]^+$. – $\text{C}_{40}\text{H}_{28}\text{Cu}_2\text{F}_6\text{N}_8\text{O}_6\text{S}_2 \cdot 0.5 \text{C}_7\text{H}_5\text{N}$ (1073.47): calcd. C 48.67, H 2.86, N 11.09; found C 48.87, H 2.72, N 11.27.

Crystal structure determinations

Crystals of **2**, **4**, and **7** suitable for X-ray diffraction were mounted in glass capillaries and investigated with a Nonius KappaCCD area detector equipped with graphite-monochromated MoK_α radiation. Table 1 lists the cell parameters and details of the data acquisition and structure refinement. Absorption corrections were applied using SCALEPACK. The structures were solved by Direct Methods (SHELXS-97) [18] and refined by full-matrix least-squares techniques against F^2 using the SHELXL-97 program system [19]. 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 . The asymmetric unit of **2** contained 0.5 molecule of disordered methylene chloride. CCDC 171340 (**7**), CCDC 171341 (**2**), and CCDC 171342 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] L. Plasseraud, H. Maid, F. Hampel, R. W. Saalfrank, *Chem. Eur. J.* **2001**, 7, 4007–4011.
- [2] a) A. Scheurer, H. Maid, F. Hampel, R. W. Saalfrank, L. Toupet, P. Mosset, R. Puchta, N. J. R. van Eikema Hommes, *Eur. J. Org. Chem.* **2005**, 2566–2574; b) R. W. Saalfrank, A. Scheurer, R. Puchta, F. Hampel, H. Maid, F. W. Heinemann, *Angew. Chem.* **2007**, 119, 269–272; *Angew. Chem. Int. Ed.* **2007**, 46, 265–268.
- [3] A. S. Batsanov, M. J. Begley, M. W. George, P. Hubberstey, M. Munakata, C. E. Russel, P. H. Walton, *J. Chem. Soc., Dalton Trans.* **1999**, 4251–4259.
- [4] For recent papers on Cu(I) complexes, see *e. g.*: a) S. A. Baudron, M. W. Hosseini, N. Kyritsakas, *New J. Chem.* **2006**, 30, 1083–1086; b) K. Saito, T. Arai, N. Takahashi, T. Tsukuda, T. Tsubomura, *Dalton Trans.* **2006**, 4444–4448; c) Q. Zhai, C. Lu, Q. Zhang, X. Wu, X. Xu, S. Chen, L. Chen, *Inorg. Chim. Acta* **2006**, 359, 3875–3887; d) J. He, Y.-G. Yin, T. Wu, D. Li, X.-C. Huang, *Chem. Commun.* **2006**, 2845–2847; e) L. R. Hanton, R. M. Hellyer, M. D. Spicer, *Inorg. Chim. Acta* **2006**, 359, 3659–3665; f) G. A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Polyhedron* **2006**, 25, 3278–3284; g) P. V. Solntsev,

- J. Sieler, H. Krautscheid, K. V. Domasevitch, *Dalton Trans.* **2004**, 1153–1158; h) R. Horikoshi, T. Mochida, H. Moriyama, *Inorg. Chem.* **2002**, *41*, 3017–3024.
- [5] L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *Inorg. Chem.* **1998**, *37*, 5941–5943.
- [6] P. Comba, C. Katsichtis, B. Nuber, H. Pritzkow, *Eur. J. Inorg. Chem.* **1999**, 777–783.
- [7] For bridging behaviour of benzo[c]cinnoline ligands, see: A. Toth, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1987**, *26*, 236–241.
- [8] R. J. Doedens, *Inorg. Chem.* **1970**, *9*, 429–436.
- [9] H.-F. Klein, M. Helwig, U. Koch, U. Flörke, H.-J. Haupt, *Z. Naturforsch.* **1993**, *48b*, 778–784.
- [10] For η^2 coordination mode of benzo[c]cinnoline ligand, see: Y. Nakayama, A. Nakaruma, K. Mashima, *Chem. Lett.* **1997**, 803–804.
- [11] H. V. R. Dias, H. V. K. Diyabalanaga, C. S. Palehepitiya Gamage, *Chem. Commun.* **2005**, 1649–1621.
- [12] E. K. Pham, L. McElwee-White, *Acta Crystallogr.* **1992**, *C48*, 1120–1121.
- [13] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.
- [14] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.
- [15] See *e.g.*: a) K. S. Min, M. P. Suh, *Eur. J. Inorg. Chem.* **2001**, 449–455; b) T. Kuroda-Sowa, M. Munakata, H. Matsuda, S.-i. Akiyama, M. Maekawa, *J. Chem. Soc., Dalton Trans.* **1995**, 2201–2208; c) L. Han, M. Hong, *Inorg. Chem. Commun.* **2005**, *8*, 406–419; d) K. V. Domasevitch, I. Boldog, E. B. Rusanov, J. Hunger, S. Blaurock, M. Schröder, J. Sieler, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1095–1100; e) W. Huang, H. Qian, *J. Mol. Struct.* **2005**, *741*, 155–158; f) C.-L. Chen, B.-S. Kang, C.-Y. Su, *Aust. J. Chem.* **2006**, *59*, 3–18; g) F. Tuna, J. Hamblin, G. Clarkson, W. Errington, N. W. Alcock, M. J. Hannon, *Chem. Eur. J.* **2002**, *8*, 4957–4964; h) X.-M. Chen, G.-F. Liu, *Chem. Eur. J.* **2002**, *8*, 4811–4817; i) R. W. Saalfrank, C. Deutscher, S. Sperner, T. Nakajima, Ayuk M. Ako, E. Uller, F. Hampel, F. W. Heinemann, *Inorg. Chem.* **2004**, *43*, 4372–4382.
- [16] M. Maekawa, M. Munakata, T. Kuroda-Sowa, Y. Nozaka, *J. Chem. Soc., Dalton Trans.* **1994**, 603–607.
- [17] R. G. Solomon, J. K. Kochi, *J. Chem. Soc., Chem. Comm.* **1972**, 559–560.
- [18] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.
- [19] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.