Self-assembly Through Non-coordinating Intermolecular Forces, Part 2 [1]. Synthesis, Crystal Structure and Packing of $[Cu_2(\mu\text{-phthalazine})_3(\text{phthalazine})_2][CF_3SO_3]_2$

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Treatment of the copper(I) trifluoromethanesulphonate toluene complex $\{[Cu(CF_3SO_3)]_2 \cdot C_6H_5Me\}$ (**1**) with phthalazine (phtz, $C_8H_6N_2$) in dichloromethane-acetonitrile solution yielded, *via* the bis(acetonitrile)tris(μ-phthalazine)dicopper(I) trifluoromethanesulphonate intermediate (**2**), the novel bis(phthalazine)tris(μ-phthalazine)dicopper(I) trifluoromethanesulphonate salt (**3**). Compound **3** was completely characterised and the molecular structure determined by single-crystal X-ray diffraction. Complex **3** crystallises in the monoclinic system, space group $C2/c$, with a = 26.9527(10), b = 10.9558(7), c = 19.2104(10) Å, β = 127.268(2)°, V = 4514.3(4) Å^3 and Z = 4. The copper(I) coordination geometry is tetrahedral, each copper centre being linked to four phthalazine molecules. Dicationic units of **3** which present an unusual paddle wheel-like shape constitute appropriate organometallic building blocks for the construction of a supramolecular solid-state architecture. The analysis of the packing of the molecules of **3** in the crystal revealed an unprecedented 2-dimensional network, resulting from intermolecular π-π and electrostatic interactions.

Key words: Copper(I), N Ligand, Organometallic Synthon, π-π Interactions, Self-assembly, Crystal Structure

Introduction

The past few years have witnessed an exponentially growing interest in the field of coordination polymers also named metal-organic coordination frameworks (MOCNs) or metal-organic frameworks (MOFs). Basically, the construction of coordination polymers is based on the coordination of metal centres by rigid multidentate organic ligands containing in most cases nitrogen and oxygen donor atoms. In addition to coordinative bonding, the participation of weak non-covalent interactions such as hydrogen bonding, π-π contacts, van der Waals and ionic forces, increases the variety of motifs of multidimensional organisation. The choice of the molecular building blocks plays a determinant role for the final properties of the synthesised materials. Coordination polymers are studied and applied more and more in catalysis [2], gas and small molecule sorption [3], molecular recognition [4], and functional solid materials elaboration [5]. Lately, two well-documented reviews highlighted in particular the engineering and the applications of coordination polymer networks [6].

The extension of this methodology to the utilisation of discrete organometallic complexes or metal clusters as building blocks, instead of simple metal ions, can lead to the formation of supramolecular organometallic coordination networks [7]. In numerous examples, the secondary non-covalent interactions, especially hydrogen bonding and π-π stacking, are the driving forces for the connection between organometallic synthons [8]. This more recent area of research is particularly promising in order to elaborate multidimensional networks with more advanced catalytic and porous properties, taking advantage of the specific properties of defined organometallic complexes [9].

In a previous study, we reported the syntheses and the crystal structures of copper(I) complexes based on pyridazine-type ligands exhibiting remarkable two- and three-dimensional organisations, resulting from intermolecular π-π stacking interactions [1]. Continuing our investigations in this field and in quest of

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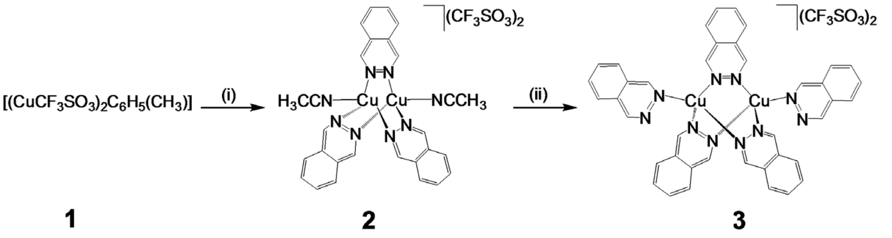


Scheme 1. Reagents and conditions: (i) phtz, CH_3CN, CH_2Cl_2, room temperature (r. t.), 1 h; (ii) phtz, 12 h, r. t., crystallisation from CH_2Cl_2/ diethyl ether.

novel non-organic synthons suitable for self-assembly through non-coordinating intermolecular forces, we describe herein the preparation, the characterisation and the solid-state arrangement of the new organometallic building block $[Cu_2(\mu\text{-phthalazine})_3(\text{phthalazine})_2][CF_3SO_3]_2$ (**3**).

Results and Discussion

Synthesis and spectroscopic characterisation

The synthetic pathway to the title compound is summarised in Scheme 1. First, the bis(acetonitrile)tris(μ-phthalazine)dicopper(I) trifluoromethanesulphonate complex, $[Cu_2(\mu\text{-phtz})_3(CH_3CN)_2][CF_3SO_3]_2$ (**2**), was prepared *in situ* in dichloromethane at r. t. from the copper(I) trifluoromethanesulphonate toluene complex, $\{[Cu(CF_3SO_3)]_2 \cdot C_6H_5Me\}$ (**1**), in the presence of a stoichiometric amount of phthalazine (phtz, $C_8H_6N_2$) and addition of acetonitrile. By using the same synthetic procedure, we reported formerly the isolation and the structural characterisation of the benzonitrile analogue of **2**, $[Cu_2(\mu\text{-phtz})_3(C_6H_5CN)_2][CF_3SO_3]_2$ [1] which consists to two tetrahedral copper(I) centres bridged by three phthalazine molecules and terminally bound to two benzonitrile ligands. In the presence of acetonitrile, we assumed by analogy a similar structure for **2**. When a supplementary amount of phthalazine was added to the dichloromethane solution of **2**, the colour of the solution turned instantaneously from yellow to deep orange. The two terminal acetonitrile ligands were replaced by two phthalazine molecules giving the new bis(phthalazine)tris(μ-phthalazine)dicopper(I) trifluoromethanesulphonate salt (**3**). Addition of diethyl ether led to the precipitation of an orange powder characterised as **3**. Crystallisation at r. t. from a mixture of dichloromethane/diethyl ether afforded single crystals suitable for an X-ray diffraction study. The IR spectrum of **3** exhibits characteristic absorptions of the phthalazine ligands at 3055, 1576, 1491, 1445, 1379, 753, and 652 cm^{-1}, while bands of the trifluoromethanesulphonate anion, in particular $\nu(CF_3)$ and $\nu(SO_3)$, are observed in the stretching region between 1000 and 1300 cm^{-1}, precisely at 1256, 1225, 1153 and 1030 cm^{-1} [10]. The ^1H NMR spectrum in $CDCl_3$ displays a broad signal at δ = 9.87 ppm and a multiplet in the range 8.25 – 7.95 ppm corresponding to the aromatic protons of the phthalazine ligands. The electrospray mass spectrum (methanol) of **3** in the positive mode displays two intense peaks at *m/z* = 471.9 (100 %) and *m/z* = 323 (68 %) which are assigned to mononuclear copper species, $[Cu(\text{phtz})_2(CF_3SO_3)]^+$

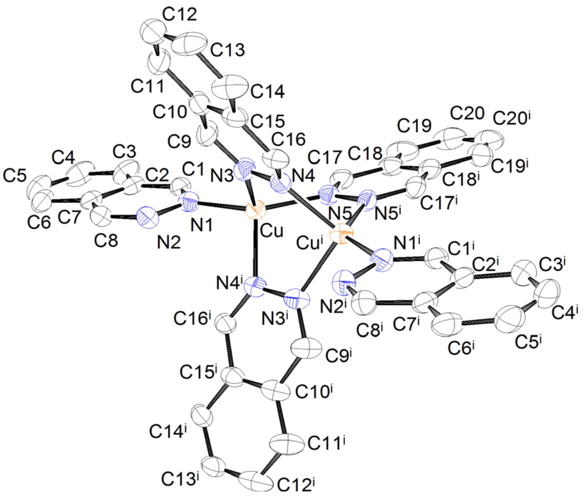


Fig. 1. ORTEP diagram of **3** with atomic numbering scheme (hydrogen atoms and counter anions ($CF_3SO_3^-$) omitted for clarity; Cu orange, N blue, C white). Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Cu–Cu^i 3.0407(14), Cu–N1 1.990(5), Cu–N5 2.012(4), Cu–N3 2.088(5), Cu–N4^i 2.086(5), N1–N2 1.387(7), N3–N4 1.376(7), N5–N5^i 1.383(9); N1–Cu–N5 131.92(19), N1–Cu–N4^i 103.78(19), N1–Cu–N3 103.56(19), N5–Cu–N4^i 106.10(18), N5–Cu–N3 105.72(19), N4^i–Cu–N3 102.36(18), N1–Cu–Cu^i 162.47(14), N3–Cu–Cu^i 65.79(14), N4^i–Cu–Cu^i 67.05(13), N5–Cu–Cu^i 65.58(13), N2–N1–Cu 109.9(4). Symmetry transformations used to generate equivalent atoms: i: $-x+1, y, -z+3/2$ (colour online).

and $[Cu(phtz)_2]^+$, respectively. The microanalytical data also confirm the composition of **3**.

Structure description

Crystallographic data and structure refinement details for **3** are summarised in Table 1. Selected bond lengths and angles are listed in the caption of Fig. 1. The solid-state structure of **3** consists of a $[Cu_2(\mu\text{-phtz})_3(phtz)_2]^{2+}$ dication surrounded by two uncoordinated $[CF_3SO_3]^-$ counter anions. An ORTEP view of the dication is shown in Fig. 1 with the labelling of atoms. The molecule exhibits twofold symmetry with a crystallographic C_2 axis located in the long axis of the [N5–N5^i] phtalazine ligand. Both copper(I) ions are triply bridged by three phthalazine ligands, and the coordination sphere is completed by a terminal phthalazine molecule. The Cu···Cu^i separation of 3.0408(14) Å is similar to that observed for the related benzonitrile salt $[Cu_2(\mu\text{-phtz})_3(C_6H_5CN)_2][CF_3SO_3]_2$ (3.050(3) Å) [1]. The copper atoms have an approximately tetrahedral geometry. The N–Cu–N angles are in the range 102.4 – 106.1° and differ slightly from the ideal tetrahedral angle (109.5°) with the exception of the N1–Cu–N5 angle which exhibits a serious deviation (131.92(19)°). The terminal phthalazine molecules are linked to the copper centres in an η^1 coordination mode (Cu–N1 = 1.990(5) Å). These terminal ligands are almost coplanar with a dihedral angle between the best least-squares planes of 4.4(1)°. The non-coordinated nitrogen atoms of phthalazine are thus situated face to face. Interestingly, the three bridging phthalazine ligands are positioned around the Cu···Cu^i vector in a threefold symmetric arrangement and are coordinated to the copper atoms in a μ-1,2 fashion (Cu–N3 = 2.088(5), Cu–N4^i = 2.086(5), Cu–N5 = 2.012(5) Å). One bridging molecule (N5–N5^i) is almost included in the plane containing the terminal phthalazine ligands (dihedral angle of 5.4(2)°), while the two other bridging ligands, (N3–N4) and (N4^i–N3^i) respectively, are situated symmetrically on both sides of the (N5–N5^i) plane with a dihedral angle of 64.0(1)°. The $CF_3SO_3^-$ counter ions are not directly coordinated to the copper(I) centres (the shortest contact is d(Cu···O) = 4.443(15) Å), in agreement with the stretching frequencies observed in the IR spectrum. However, the trifluoromethanesulphonate anions are held in place by weak interactions to the bridging phthalazine ligands through CH···O contacts (distances in the range 3 – 3.5 Å).

Table 1. Crystal structure data for **3**.

Formula	$C_{40}H_{30}Cu_2N_{10}$ $2(CF_3SO_3)$
M_r	1075.96
Cryst. size, mm^3	$0.25 \times 0.12 \times 0.07$
Crystal system	monoclinic
Space group	*C*2/*c*
a, Å	26.9527(10)
b, Å	10.9558(7)
c, Å	19.2104(10)
β, deg	127.268(2)
V, Å^3	4514.3(4)
Z	4
D_{calcd}, g cm^{-3}	1.583
radiation; λ, Å	MoK_α; 0.71073
μ(MoK_α), cm^{-1}	1.119
F(000), e	2176
hkl range	$-33 \le h \le 34$
	$-14 \le k \le 12$
	$-24 \le l \le 24$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.65
Refls. collected	7428
Independent Refls.	4986
R_{int}	0.0392
Refls. with $[I \ge 2\sigma(I)]$	3486
Data / restraints / parameters	4986 / 26 / 292
Refinement method	Full-matrix least-squares on F^2
$R1^a/wR2^b$ $[I \le 2\sigma(I)]$	0.084/0.215
$R1^a/wR2^b$ (all data)	0.119/0.242
GoF $(F^2)^a$	1.039
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	1.76/−1.12

[a] $R1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2 / \Sigma[w(F_o{}^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o{}^2) + 40.8069P + (0.1141P)^2]$ where $P = (\mathrm{Max}(F_o{}^2,0) + 2^*F_c{}^2)/3$; [c] GoF = $[\Sigma w(F_o{}^2 - F_c{}^2)^2 / (N_o - N_v)]^{1/2}$.

Crystal packing

Non-covalent intra- and intermolecular interactions, and specially arene-arene interactions are preponderant in biological processes, recognised in particular to play an important role in the folding and the thermal stability of proteins [11]. The double helix structure of DNA constitutes one of the most representative examples of π-π stacking in nature. A well-documented survey related to the interactions with aromatic rings in chemical and biological recognition has been published by Diederich and co-workers [12]. In the field of crystal engineering, the role of interactions between aromatic rings has been known for a long time [13] and continues to be intensively studied and used for the construction of propagating networks [14].

Analysis of the packing of molecules of **3** in the crystal revealed a 2-dimensional network generated through intermolecular arene-arene stacking interactions between N-heterocyclic ligands, and through electrostatic interactions. The resulting solid-state ar-

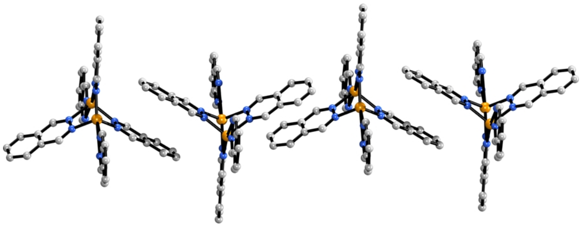


Fig. 2. Perspective view of **3** showing a 1D chain formed through face-to-face π-π phthalazine interactions [DIAMOND presentation, hydrogen atoms and counter anions ($CF_3SO_3^-$) omitted for clarity; Cu orange, N blue, C grey (colour on line)].

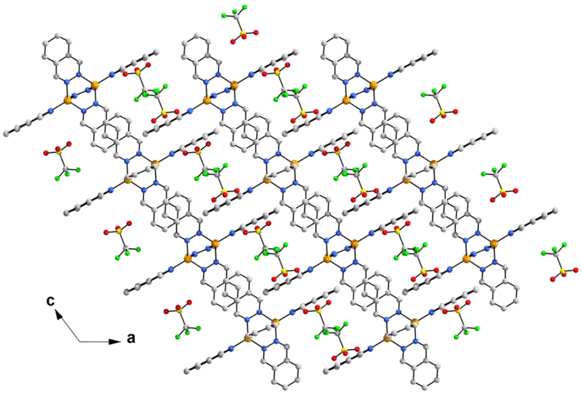
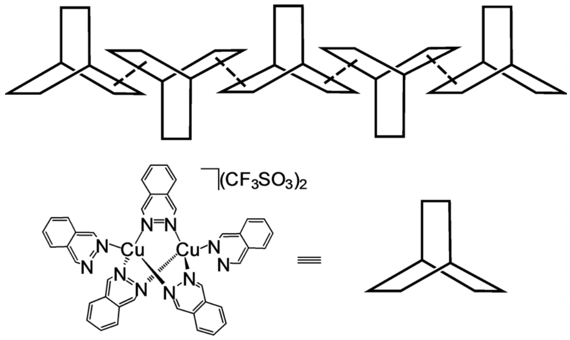


Fig. 3. Extended 2D network of **3** in the *ac* plane showing the counter anions ($CF_3SO_3^-$) intercalated between the chains based on dicationic units [DIAMOND presentation, hydrogen atoms omitted for clarity; Cu orange, N blue, C grey, O red, fluorine green, S yellow (colour on line)].

chitecture can be described according to two successive levels of organisation, a one dimensional (1D) chain extended to a two-dimensional (2D) network as displayed in Figs. 2 and 3, respectively. First, dicationic units of **3** are arranged in a 1D chain based on face-to-face π-π intermolecular stacking between bridging phthalazine molecules.

Two phthalazine ligands of each dicopper(I) dication interact with two other phthalazine molecules of neighbouring units of **3** leading to the propagation of the chain in the direction of the *c* axis. Both aromatic rings of each phthalazine ligand are implicated in π-π contacts and positioned face-to-face. The interplanar distances between the rings are 3.32(1) Å. The aromatic ligands are slipped by 1.16 Å (slip angle 19.3°) and the ring-centroid to ring-centroid distances are 3.52 Å. These data are in agreement with the range of parameters observed previously for face-to-face π-π stacking in metal complexes with aromatic nitrogen-containing ligands. For face-to-face interactions, the centroid-centroid distance is between 3.3 and 3.8 Å, and the slip angle is given in the range 16–40° [15]. Interestingly, the building blocks of **3** fit perfectly so that the bridging phthalazine ligand non-concerned in the π-π stacking and corresponding to the phtalazine which contains the C_2 axis lie alternately above and below the propagation chain axis in a syndiotactic manner. A schematic representation of the paddle wheel-like shape of **3** and the construction of the 1D chain are depicted in Scheme 2. To our knowledge, such an arrangement of organometallic building blocks through arene-arene interactions has not been reported in the literature so far.



Scheme 2. Schematic representation of **3** in a paddle wheel-like shape, and the construction of the 1D chain generated through face-to-face π-π interactions (indicated as dashed lines).

Furthermore, the 1D chains are linked together to give a 2D network which lies in the *ac* plane with a stacking orthogonally to the *b* axis. The two-dimensional architecture probably results from the action of several non-coordinating forces making its description more difficult than for the 1D level of organisation. First, we assume that the trifluoromethanesulphonate anions which are intercalated between the π-π stacking-based chains provide attractive electrostatic interactions between the 1D chains. In addition, a weak contribution of interactions based on parallel displaced π-π stacking between the terminal phthalazine ligands and the (N5–N5^{i}) bridging molecules of neighbouring chains is also discernible. Indeed, the interplanar distance between the two external rings of the phthalazines is 3.46(1) Å, and the centroid-centroid distance and the slip angle between the ring planes are 4.51 Å and 40°, respectively (slippage distance = 2.89 Å), that demonstrate the possible offset π-stacked character of this interaction. Again, these values are in the range usually given for this type of interaction [15].

Up to now, such a two-dimensional organometallic architecture driven by electrostatic and π-π interactions has relatively seldom been described. A 2D network related to that of **3**, constructed in a self-assembly of a nickel(II) macrocyclic complex containing pyridyl pendant rings was previously published by Suh and coworkers [8b].

In summary, we have synthesised and characterised a new dinuclear copper(I) complex based on phthalazine-type ligands and presenting an unusual paddle wheel-like shape. Discrete molecules of **3** proved to be suitable as organometallic building blocks for the assembly of 1D chains driven by π-π interactions between bridging phthalazine ligands. A 2D network based on electrostatic and π-π interactions between terminal and bridging phthalazine ligands is formed. Further studies based on this approach and taking advantage of the appropriate geometry of phthalazine-based copper(I) complexes are currently in progress.

Experimental Section

All reactions were carried out under dry argon using Schlenk tube techniques [16]. The organic solvents were refluxed over appropriate desiccants, distilled, and saturated with argon prior to use. Chemicals were purchased from Acros Organics and used without further purification. The starting compound $\{[Cu(CF_3SO_3)]_2 \cdot C_6H_5Me\}$ was synthesised from trifluoromethanesulphonic acid anhydride and copper(I) oxide in toluene according to a published method [17]. The ^{1}H NMR experiments were run at 298 K in $CDCl_3$ on a Bruker Avance 300 spectrometer at 300.131 MHz, and calibrated with Me_4Si as an internal standard. Chemical shift δ values are given in ppm. The resonance multiplicity is indicated as s (singlet) and m (multiplet). IR spectra were recorded on a Bruker Vector 22 instrument equipped with a Specac Golden Gate™ ATR device. The ES mass spectrum was obtained on a Bruker microOTOF-Q instrument using a methanol mobile phase. Elemental analyses (C, H, N, S) were performed at the Institut de Chimie Moléculaire de l'Université de Bourgogne, Dijon.

$[Cu_2(\mu\text{-phtz})_3(\text{phtz})_2]\,[CF_3SO_3]_2$ (**3**)

Freshly prepared $\{[Cu(CF_3SO_3)]_2 \cdot C_6H_5Me\}$ (**1**) (0.711 g, 2.75 mmol) was dissolved in dichloromethane (5 mL), and phthalazine (0.536 g, 4.13 mmol) was added with stirring, leading to the formation of a yellow precipitate. Then 5 mL of acetonitrile was added, and a clear yellow solution was immediately formed. After stirring at r. t. for 1 h, an additional amount of phthalazine (0.356 g, 2.75 mmol) was introduced, and the colour of the solution turned from yellow to deep orange. The solution was again vigorously stirred for 12 h and then concentrated under vacuum to half volume. The addition of 20 mL of diethyl ether precipitated a crude orange powder which was filtered off, washed with additional diethyl ether and dried under vacuum (1 g, 65 % yield). Orange single crystals of **3** suitable for X-ray structure determination were grown from a mixture of dichloromethane/diethyl ether at r. t. – IR: ν = 3055w, 1576m, 1491m, 1445m, 1379s, 1314w, 1256vs, 1225s, 1153s, 1030vs, 842s, 753vs, 652s, 635vs cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 9.87 (br s, 10H, phtz), 8.25 – 7.95 (m, 20H, phtz). – MS: m/z (%) = 471.9 (100) $[Cu(phtz)_2(CF_3SO_3)]^+$, 323 (68) $[Cu(phtz)_2]^+$. – $C_{42}H_{30}Cu_2F_6N_{10}O_6S_2$ (1075.96): calcd. C 46.88, H 2.81, N 13.02, S 5.96; found C 46.42, H 3.12, N 13.44, S 6.24.

X-Ray structure determination

Suitable single crystals of **3** were obtained by slow evaporation of the solvent at r. t. from a solution in a mixture of dichloromethane/diethyl ether. Diffraction data were collected on a Nonius Kappa CCD instrument (MoK_α radiation, λ = 0.70173 Å) at 115 K. The structure was solved using Direct Methods (SIR92) [18] and refined with full-matrix least-squares methods based on F^2 (SHELX-97) [19] with the aid of the WINGX program [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters except for trifluoromethanesulphonate anions. Hydrogen atoms were included in their calculated positions and refined with a riding model. The trifluoromethanesulphonate anions were found to be disordered over two positions with occupation factors converging to 0.58 : 0.42 and isotropically refined with geometrical restraints. Crystallographic parameters are summarised in Table 1.

CCDC 693281 contains 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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