Isolation and X-Ray Characterization of $\{[\text{Phthalazinium}](CuCl_2)\}_\infty$: A New Example of a Dichlorocuprate(I) Presenting a Rare Staircase Chain Structure

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70th birthday

Air-sensitive complexes $[Cu_2(\mu\text{-phtz})_3(PR_3)_2][CF_3SO_3]_2$ (phtz = $C_8H_6N_2$), **3** (R = phenyl) and **4** (R = benzyl) have been synthesized from $\{[Cu(CF_3SO_3)]_2{\cdot}C_6H_5Me\}$ (**1**) at room temperature, in acetonitrile solution, after successive additions of stoichiometric amounts of phthalazine (phtz) and triphenylphosphine and tribenzylphosphine, respectively. The dissolution of **4** in an excess of benzyl chloride gave rise to the slow formation of orange needles, characterized by an X-ray crystallographic analysis as the title compound, $\{[\text{phthalazinium}](CuCl_2)\}_\infty$ (**5**). The solid-state structure of **5** can be described as a one-dimensional anionic chain, $[(CuCl_2)^-]_\infty$, presenting a rare staircase shape with terminal chloride ligands. The negative charges are compensated by monoprotonated phthalazinium cations $[\text{phtzH}]^+$ which are stacked through π-π interactions between N-heterocyclic rings, and are also in N-H hydrogen bonding interaction with the terminal chloride ligands of the anionic chain. The formation of **5** was unexpected and can be explained by the dechlorination of benzyl chloride molecules.

Key words: Copper(I), Phthalazine Ligand, Organic-Inorganic Hybrid Compound, Non-coordinating Interactions, Crystal Structure

Introduction

In the past, we published the syntheses and the crystal structures of complexes based on pyridazine-type ligands exhibiting remarkable one-dimensional infinite chains [1] (Fig. 1a) as well as supramolecular structures resulting from intermolecular π-π stacking interactions (Fig. 1b) [2]. Afterwards, we have reported the preparation of a new dinuclear copper(I) complex based on phthalazine-type ligands and presenting an unusual paddle wheel-like shape suitable for the construction of a two-dimensional network through non-coordinating intermolecular forces (Fig. 1c) [3].

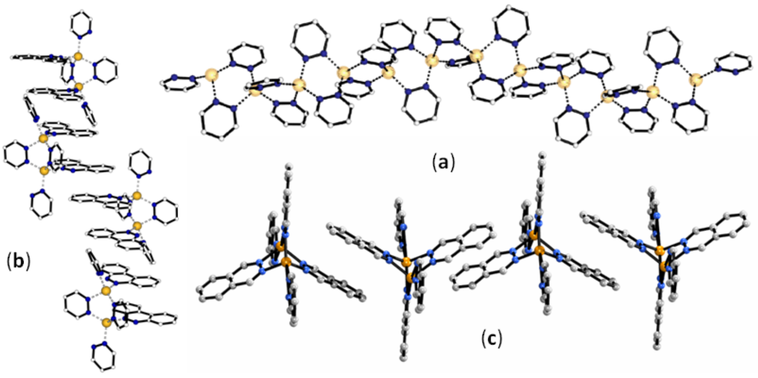
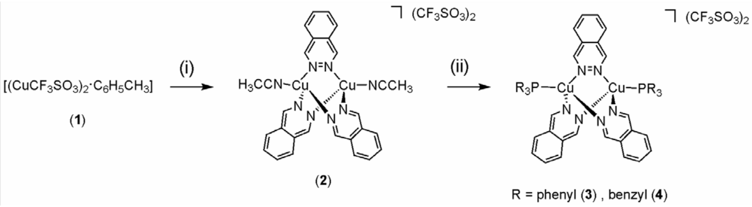


Fig. 1. Previous examples of extended structures based on diazine-bridged copper(I) complexes: (a) $^{1}_{\infty}\{[Cu(\mu\text{-pydz})_2][PF_6]\}$ [1], (b) $[Cu_2(\mu\text{-pydz})_2(\text{pydz})_2(\text{benzo[c]cinnoline})_2]\ [PF_6]_2$ [2], and (c) $[Cu_2(\mu\text{-phtz})_3(\text{phtz})_2][CF_3SO_3]_2$ [3] (pydz = pyridazine, phtz = phthalazine).



Scheme 1. Reagents and conditions: (i) phtz, CH_3CN, CH_2Cl_2, room temperature (r. t.), 1 h; (ii) PR_3, 2 h, r. t.

Continuing our investigations in the field of diazine-bridged copper(I) complexes, we describe herein the preparation of bis(triorganophosphine)tris-(μ-phthalazine)dicopper(I) trifluoromethanesulfonate salts, $[Cu_2(\mu\text{-phtz})_3(PR_3)_2][CF_3SO_3]_2$, from the copper(I) trifluoromethanesulfonate toluene complex and phthalazine and a triorganophosphine (PPh_3 and PBz_3). In our attempts of crystallization, and rather amazingly, the dissolution of the tribenzylphosphine derivative in benzyl chloride gave rise after several days to the isolation of the unexpected one-dimensional organic-inorganic hybride polymer, $\{[\text{phthalazinium}](\text{CuCl}_2)\}_\infty$, exhibiting a staircase chain structure. Until now, such polymeric frameworks implicating terminally bound halogen ligands were rarely observed for halocuprate(I) derivatives. To our knowledge, only one example has been recently reported in the literature by C. Janiak and coworkers [4]. In addition, the formation of $\{[\text{phthalazinium}](\text{CuCl}_2)\}_\infty$ from the starting salt $[Cu_2(\mu\text{-phtz})_3(PBz_3)_2][CF_3SO_3]_2$ was unpredicted and can be explained by the dehalogenation of benzyl chloride molecules according to a Wurtz-type reaction.

Results and Discussion

Synthesis

The synthetic pathway to compounds **3** and **4** is summarized in Scheme 1. First, the bis(acetonitrile)-tris(μ-phthalazine)dicopper(I) trifluoromethanesulfonate 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) trifluoromethanesulfonate 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. When stoichiometric amounts of triphenylphosphine (PPh_3) or tribenzylphosphine (PBz_3) were then added to the dichloromethane solution of **2**, the two terminal acetonitrile ligands were easily replaced giving the new bis(triorganophosphine)tris(μ-phthalazine)dicopper(I) trifluoromethanesulfonate salts **3** and **4**, respectively. Addition of diethyl ether to the solution of **3** led to the precipitation of a fine yellow powder characterized as $[Cu_2(\mu\text{-phtz})_3(PPh_3)_2][CF_3SO_3]_2$. Crystallization at r. t. from a biphasic mixture of dichloromethane/toluene afforded yellow single crystals. Unfortunately, owing to a severe disorder of the trifluoromethanesulfonate anions and despite several attempts to solve the X-ray crystallographic structure of **3**, the result is not yet publishable. However, the structural data regarding the cationic moiety are sufficient to confirm the proposed structure depicted in Fig. 1, which corresponds to two copper atoms bridged by three phthalazine molecules in a paddle wheel-like fashion and terminally coordinated by two PPh_3 ligands. In addition to characteristic absorptions of the phthalazine and triphenylphosphine ligands, the IR spectrum exhibits the stretching bands of trifluoromethanesulfonate anions, in particular $\nu(CF_3)$ and $\nu(SO_3)$ which are observed precisely at 1261, 1223, 1143, and 1029 cm^{-1} [5]. Well-soluble in halogenated solvents, salt **3** was fully characterized by multinuclear NMR spectroscopy. In the ^{19}F NMR spectrum, in CD_2Cl_2, the signal of the trifluoromethanesulfonate anions is situated at $\delta = -79.06$ ppm. The ^1H-NMR spectrum displays a singlet at $\delta = 9.92$ ppm and two multiplets in the range 8.25 – 7.95 and 7.75 – 7.50 ppm corresponding to the aromatic protons of phthalazine and triphenylphosphine ligands. The $^{31}P\{^1H\}$-NMR spectrum reveals a broad signal at $\delta = -4.63$ ppm, weakly downfield shifted with respect to the signal of free PPh_3 ($\delta = -5.55$ ppm).

The analogous tribenzylphosphine complex, $[Cu_2(\mu\text{-phtz})_3(PBz_3)_2][CF_3SO_3]_2$ (**4**), was prepared in the same way using PBz_3. Rapidly, the addition of PBz_3 to a dichloromethane solution of **2** led to the precipitation of a pale-yellow powder characterized thereafter as being **4**. Compound **4** is insoluble in most usual organic solvents. Therefore, its characterization in solution has remained limited. However, the IR fingerprint of **4** is similar to that of **3** and suggests a comparable paddle wheel-like structure (Scheme 1). In quest of a suitable solvent for crystallization, we found that salt **4** was slightly soluble in an excess of benzyl chloride giving a clear yellow solution. Crystallization attempts by vapor diffusion of toluene into a saturated benzyl chloride solution of **4** gave rise, after several days, to the growth of orange crystalline needles. However, the IR spectrum obtained of the crystals differed from that of **4**. In particular, in the range 1000 – 1300 cm^{-1}, no intense $CF_3SO_3^-$ absorptions were observed, suggesting the isolation of a new compound. The X-ray crystallographic analysis on suitable single crystals confirmed an unexpected structure and revealed an organic-inorganic hybrid compound characterized finally as $\{[\text{phthalazinium}](\text{CuCl}_2)\}_\infty$ (**5**).

Table 1. Crystal structure data for **5**.

Formula	$C_8H_7N_2CuCl_2$
M_r	265.60
Crystal size, mm^3	0.05 × 0.03 × 0.03
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	3.8589(3)
b, Å	21.957(1)
c, Å	10.7787(9)
β, deg	94.775(2)
V, Å^3	910.10(11)
Z	4
D_{calcd}, g cm^{-3}	1.94
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	2.9
$F(000)$, e	528
Radiation; λ, Å	$\text{Mo}K_\alpha$; 0.71073
hkl range	$-5 \le h \le 5$; $-17 \le k \le 28$; $-13 \le l \le 13$
$((\sin\theta)/\lambda_{\max}$, Å^{-1}	0.65
Refls. collected / independent / R_{int}	3210 / 2011 / 0.0328
Refls. with $[I \ge 2\sigma(I)]$	1743
Data / ref. parameters	2011 / 118
Refinement method	Full-matrix least-squares on F^2
$R1^a$ / $wR2^b$ $[I \ge 2\sigma(I)]$	0.0562 / 0.0986
$R1^a$ / $wR2^b$ (all data)	0.0460 / 0.0923
GoF $(F^2)^c$	1.094
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.52 / −0.77

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (4.9240P)^2 + 0.0063P]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] GoF = $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

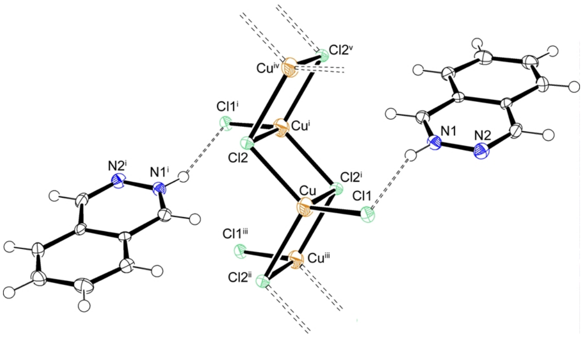


Fig. 2. Staircase chain structure of **5** (ORTEP diagram) with atomic numbering scheme [Cu orange, Cl green, N blue, C white (color on line)]. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Cu–Cl1 2.2553(10), Cu–Cl2 2.3758(11), Cu–Cl2^{i} 2.5353(11), Cu–Cl2^{ii} 2.3913(11), Cu–Cu^{i} 3.2415(11), Cu–Cu^{iii} 3.0424(12), N1–N2 1.362(4), N1(H1N)···Cl(1) 3.007(3); Cl1–Cu–Cl2 121.56(4), Cl1–Cu–Cl2^{ii} 111.71(4), Cl2–Cu–Cl2^{ii} 108.09(4), Cl1–Cu–Cl2^{i} 112.09(4), Cl2–Cu–Cl2^{i} 97.46(4), Cl2^{ii}–Cu–Cl2^{i} 103.79(3), Cl1–Cu–Cu^{iii} 127.17(4), Cl2–Cu–Cu^{iii} 110.63(4), Cl2^{ii}–Cu–Cu^{iii} 54.03(3), Cl2^{i}–Cu–Cu^{iii} 49.76(3), Cu–Cl2–Cu^{iv} 108.09(4), Cu–Cl2–Cu^{i} 82.54(4), Cu^{iv}–Cl2–Cu^{i} 76.21(3). Symmetry transformations used to generate equivalent atoms: i: $1-x, -y, -z$; ii: $x-1, y, z$; iii: $-x, -y, -z$; iv: $1+x, y, z$; v: $2-x, -y, -z$.

Crystal structure of $\{[\textit{phthalazinium}](\textit{CuCl}_2)\}_\infty$

Crystallographic data and refinement details are summarized in Table 1. Selected bond lengths and angles are listed in the caption of Fig. 2. The solid-state structure consists of monoprotonated stacked phthalazinium cations, $[\text{phtzH}]^+$, and an infinite anionic dichlorocuprate(I) chain, $[(\text{CuCl}_2)^-]_\infty$. An ORTEP view is shown in Fig. 2 with a labelling of the atoms. All copper atoms of **5** are four-coordinated by chloride ligands in a distorted tetrahedral geometry. One chlorine atom is located in a terminal position [Cu–Cl1 = 2.2553 (10) Å] and three are triply bridging the copper centers [Cu–Cl2 = 2.3758 (11), Cu–Cl2^{i} = 2.5353 (11) and Cu–Cl2^{ii} = 2.3913 (11) Å] and allow the propagation of the polymeric structure parallel to the crystallographic a axis. The resulting infinite inorganic framework, $[(\text{CuCl}_2)^-]_\infty$ can be described as a staircase chain arrangement. Two distinct Cu···Cu interatomic distances [Cu–Cu^{i} 3.2415(11), Cu–Cu^{iii} 3.0424(12) Å] are measured and are longer than the van der Waals sum of radii of Cu(I) (2.8 Å). Interestingly, the terminal Cl ligands can be viewed as positioned in a syndiotactic manner along the copper-based chain. Fascinatingly, dihalocuprate(I) compounds enjoy a diversity of solid-state structures, from molecular units to complex clusters and 1D-polymeric frameworks. Up to now, a large number of X-ray structures presenting various shapes have already been published and compiled in three different reviews [6]. However, and confirmed by an updated CCDC query, it appears that dihalocuprates(I) associated with organic cations rarely exhibit a staircase chain with terminal halides. Recently, C. Janiak and coworkers reported such a structure for a piperazinium dibromocuprate(I) also described as being a *cis* edge-sharing of arrangement tetrahedral [4]. To our knowledge, $\{[\text{phthalazinium}](CuCl_2)\}_\infty$ (**5**) constitutes the first example of a dichlorocuprate(I) presenting a staircase chain structure and thus expands the existing structural diversity of halocuprates(I).

To compensate the negative charge of the $[(CuCl_2)^-]_\infty$ anionic chains, the framework of **5** is completed by monoprotonated phthalazium cations, $[\text{phtzH}]^+$ which are engaged in two different types of non-coordinating forces. First, the N-heterocyclic rings are stacked along the *a* axis through slipped face-to-face π-π interactions. The interplanar distances between the rings are 3.40(2) Å with a slippage distance of 1.83 Å (slip angle 28.3°). The ring-centroid to ring-centroid distances are 3.859 Å. These data are in agreement with the range of parameters generally observed previously for such slipped face-to-face π-π stacking interactions [7]. Furthermore, the NH function of each phthalazinium cation is also in hydrogen bonding interaction with a terminal chloride of the anionic $[(CuCl_2)^-]_\infty$ framework [N(H)···Cl distance = 3.007(3) Å, N(H)···Cl angle = 157.58°] [8]. Consequently, two self-organized phthalazinium stacks are positioned on each side and parallel to the inorganic chains. A DIAMOND view of the resulting organic-inorganic network is depicted in Fig. 3. From a crystal packing point of view, the organization of $[\text{phtzH}]^+$ cations in stacks through π-π interactions, as well as the existence of NH-Cl hydrogen bonding, are assuredly the driving force leading to the polymeric staircase structure of $[(CuCl_2)^-]_\infty$. In the past, this concept and especially the different parameters determining the morphology of halocuprates(I) have been discussed by Hasselgren Arnby, Jagner, and Dance [6c].

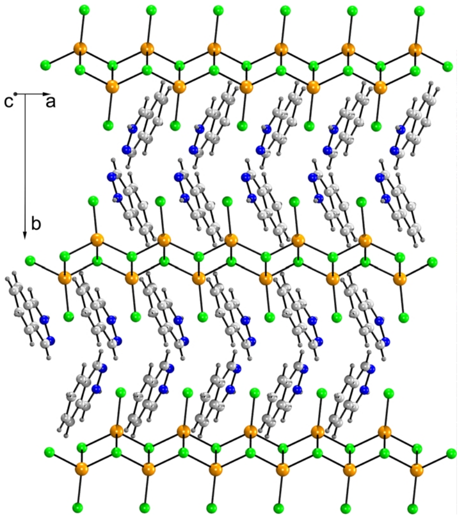


Fig. 3. Network and packing diagram for **5**, highlighting the π-π stacking of phthalazinium cations and their orientation toward $[(CuCl_2)^-]_\infty$ chains [DIAMOND presentation; Cu orange, Cl green, N blue, C grey (color on line)].

Mechanistic considerations

In addition to the structural aspect, the formation mechanism of $\{[\text{phthalazinium}](CuCl_2)\}_\infty$ is also interesting. Indeed, the isolation of **5** was unexpected and occurred when the dinuclear complex $[Cu_2(\mu\text{-phtz})_3(PBz_3)_2][CF_3SO_3]_2$ (**4**) was dissolved in benzyl chloride (BzCl). Our hypothesis to explain the formation of $[(CuCl_2)^-]_\infty$ anions and phthalazinium cations implies a dechlorination reaction of BzCl (the only source of chloride). Thus, complex **4** acts as a chloride acceptor leading to the anionic $[(CuCl_2)^-]_\infty$ inorganic polymer. Preliminary GC and GC/MS investigations on the mother liquor of **5** have shown the presence of free tribenzylphosphine and phthalazine corroborating the structure of **5** which requires the liberation of PBz_3 and phtz ligands from **4**. Further work is in progress to determine accurately the nature of organic products generated from the dechlorination reaction, as well as the origin of the proton of the $[\text{phtzH}]^+$ cations.

Copper(I) complexes have been known for a long time to promote in particular the homo-coupling of alkyl halides (Wurtz-type reaction), and numerous publications have focused on the dechlorination of benzyl chloride in various reaction media [9]. However, up to now, the general dehalogenation mechanism remains still unknown [10]. Several mechanistic pathways have been postulated. One of them, supported by computational studies, propose the *in situ* formation of a Cu(III) halide species playing the role of a key intermediate, but no structural evidence has yet been obtained [11]. Moreover, to date, only few copper species have been isolated and structurally characterized at the end of the coupling reactions [9c, 12]. Therefore, the isolation of $\{[\text{phthalazinium}](CuCl_2)\}_\infty$ (**5**) as single crystals and its X-ray crystallographic investigation can be viewed as a new clue for the quest of a better understanding of the possible mechanism.

Experimental Section

All reactions were carried out under dry argon using Schlenk tube techniques [13]. The organic solvents were refluxed over appropriate dessicants, distilled, and saturated with argon prior to use. Phthalazine (phtz, Sigma-Aldrich), triphenylphosphine (PPh_3, Sigma-Aldrich), tribenzylphosphine (PBz_3, Interchim), and benzyl chloride (BzCl, Sigma-Aldrich) were used without further purification. The starting compound $\{[Cu(CF_3SO_3)]_2{\cdot}C_6H_5Me\}$ was synthesized from trifluoromethanesulfonic acid anhydride (Sigma-Aldrich) and copper(I) oxide (Fluka) in toluene according to a published method [14]. The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{19}F NMR experiments were carried out on a Bruker Avance 300 spectrometer and the spectra calibrated with Me_4Si (^1H, $^{13}C^1H$), H_3PO_4 ($^{31}P\{^1H\}$, 85 % in water) and CCl_3F (^{19}F) as internal standards. 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^{TM} ATR device. Elemental analyses (C, H, N, S) were performed at the Institut de Chimie Moléculaire de l'Université de Bourgogne, Dijon.

*Synthesis of $[Cu_2(\mu\text{-phtz})_3(PPh_3)_2]\,[CF_3SO_3]_2$ (**3**)*

Freshly prepared $\{[Cu(CF_3SO_3)]_2{\cdot}C_6H_5Me\}$ (**1**) (0.295 g, 1.1 mmol) was dissolved in dichloromethane (20 mL), and phthalazine (0.222 g, 1.7 mmol) was added with stirring, leading to the formation of a yellow precipitate. Then 1 mL of acetonitrile was added, and a bright orange-yellow solution was immediately formed. After stirring at r. t. for 1 h, a stoichiometric amount of PPh_3 (0.299 g, 1.1 mmol) was introduced, and the color of the solution turned from yellow to deep-orange. The solution was again vigorously stirred for 2 h, and then concentrated under vacuum to half volume. The addition of 20 mL of diethyl ether precipitated a crude pale-yellow powder which was filtered off, washed with additional diethyl ether and dried under vacuum (0.476 g, 65 % yield). Crystallization of **3** was achieved from a mixture of dichloromethane/toluene at r. t. – IR: ν = 3056w, 1581w, 1479m, 1435m, 1381m, 1379s, 1261vs, 1223s, 1143s, 1095s, 1029vs, 746vs, 694s, 634vs, 571m, 523s, 520s cm^{-1}. – ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ = 8.92 (br s, 6H, phtz), 8.08 – 7.99 (m, 6H, phtz), 7.75 – 7.50 (m, 36H, phtz and PPh_3). – $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): $\delta = -4.63$ (br s, PPh_3). – $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2, 298 K): δ = 121.15 (CF_3, q, $^1J_{C-F}$ = 322 Hz), 127.26, 127.70, 130.27, 130.40, 131.36, 131.76, 131.81, 134.22, 134.42, 136.05, 154.82. – ^{19}F NMR (282.37 MHz, CD_2Cl_2, 298 K): $\delta = -79.06$ (s, $CF_3SO_3^-$). – $C_{62}H_{48}Cu_2F_6N_6O_6P_2S_2{\cdot}{}^1\!/_2CH_2Cl_2$ (1382.73): calcd. C 54.29, H 3.57, N 6.08, S 4.64; found C 54.25, H 3.79, N 6.17, S 4.00.

*Synthesis of $[Cu_2(\mu\text{-phtz})_3(PBz_3)_2]\,[CF_3SO_3]_2$ (**4**)*

Compound **4** was prepared similarly to **3**, from a mixture of $\{[Cu(CF_3SO_3)]_2{\cdot}C_6H_5Me\}$ (0.288 g, 1.1 mmol) and phthalazine (0.217 g, 1.7 mmol) in dichloromethane (20 mL) in the presence of acetonitrile (1 mL). The addition of PBz_3 (0.339 g, 1.1 mmol) led immediately to the precipitation of a yellow powder (0.646 g, 81 % yield) insoluble in most usual organic solvents. – IR: ν = 3061w, 1621w, 1601w, 1581w, 1496m, 1452m, 1421w, 1383m, 1273vs, 1224s, 1148s, 1095s, 1066m, 1031s, 919m, 843m, 763s, 734s, 702vs, 636vs, 573m, 517m cm^{-1}. – $C_{68}H_{60}Cu_2F_6N_6O_6P_2S_2{\cdot}{}^1\!/_2CH_2Cl_2$ (1466.89): calcd. C 56.09, H 4.19, N 5.73, S 4.37; found C 55.83, H 3.78, N 6.21, S 5.91.

*Isolation of $\{[phtzH](CuCl_2)\}_\infty$ (**5**)*

Benzyl chloride (8 mL) was added to freshly prepared $[Cu_2(\mu\text{-phtz})_3(PBz_3)_2]\,[CF_3SO_3]_2$ (**4**) (0.144 g, 0.1 mmol). The solution was vigorously stirred for 2 h at r. t., and then the resulting yellow solution was filtered. Compound **5** was isolated as orange crystalline needles by vapor diffusion of toluene into the benzyl chloride solution, after several days at r. t. – IR: ν = 3072w, 3024w, 2984w, 2361m, 1604w, 1487w, 1452w, 1427w, 1384m, 1268m, 1225m, 1009m, 971m, 950m, 884s, 865s, 805s, 771s, 754s, 639s, 518s cm^{-1}. – $C_8H_7CuN_2Cl_2$ (265.61): calcd. C 36.17, H 2.65, N 10.57; found C 36.91, H 1.89, N 10.31.

X-Ray structure determination

Suitable single crystals of **5** were measured on a Nonius Kappa CCD diffractometer (MoK_α radiation, λ = 0.70173 Å), and diffraction data were collected at 115 K. The structure was solved using Direct Methods (SIR 92) [15] and refined with full-matrix least-squares methods based on F^2 (SHELX-97) [16] with the aid of the WINGX suite of programs [17]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their calculated positions and refined with a riding model. Crystallographic parameters are summarized in Table 1. Programs used for the representation of the molecular and crystal structures: ORTEP [18], DIAMOND [19].

CCDC 752880 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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