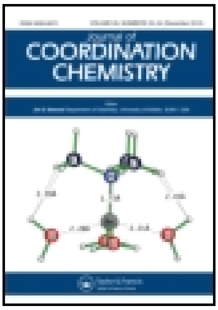

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Syntheses, crystal structures, and luminescence of coordination polymers $[Cu(\mu\text{-}Br)(\mu\text{-}phpzm)]_n$, $[\{Cu(\mu\text{-}SCN)\}_2(\mu\text{-}phpzm)]_n$, and $[(phpzm)Cu(\mu\text{-}CN)]_n$ (phpzm = bis(4-phenylpyrazol-1-yl)methane)

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Syntheses, crystal structures, and luminescence of coordination polymers $[Cu(\mu\text{-}Br)(\mu\text{-phpzm})]_n$, $[\{Cu(\mu\text{-}SCN)\}_2(\mu\text{-phpzm})]_n$, and $[(phpzm)Cu(\mu\text{-}CN)]_n$ (phpzm = bis(4-phenylpyrazol-1-yl)methane)

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Solvothermal reactions of CuX (X = Br, SCN, CN) with bis(4-phenyl-pyrazol-1-yl)methane (phpzm) gave two 2-D coordination polymers, $[Cu(\mu\text{-}Br)(\mu\text{-phpzm})]_n$ (**1**) and $[\{Cu(\mu\text{-}SCN)\}_2(\mu\text{-phpzm})]_n$ (**2**), and a 1-D coordination polymer, $[(phpzm)Cu(\mu\text{-}CN)]_n$ (**3**). Compounds **1**–**3** were characterized by elemental analysis, IR spectra, and X-ray crystallography. Compounds **1** and **2** have 2-D networks in which split-stair $[Cu(\mu\text{-}Br)]_n$ chains (**1**) or staircase-like $[Cu(\mu\text{-}SCN)]_n$ double chains (**2**) are linked by μ-phpzm bridges. Compound **3** consists of a zigzag chain formed by linking [Cu(phpzm)] fragments *via* cyanide bridges. Luminescence properties of **1**–**3** along with phpzm in the solid state at ambient temperature were also investigated.

Keywords: Solvothermal synthesis; Crystal structure; Copper(I) complex; Bis(4-phenyl-dimethylpyrazol-1-yl)methane; Luminescence

1. Introduction

Copper(I) halide and pseudohalide complexes of various poly(pyrazolyl)borates [1–8] or poly(pyrazolyl)alkanes [9–21] have attracted attention due to structural diversity [10, 15, 18, 22] and potential applications in catalysis [3, 6], electrical conductivity [5], optics [2, 11, 12], and biology [7, 8, 14, 20]. Among those poly(pyrazolyl) ligands, bis(pyrazolyl)methane has reacted with CuX (X = Cl, Br, I, CN, SCN) to produce monomeric [23], dimeric [24], or polymeric complexes [24b, 25]. We have been interested in the syntheses, structures, and luminescent properties of Cu(I) complexes with various bi(pyrazolyl)methane ligands [10, 11, 24, 25]. For example, reactions of Cu(I) with bis(3,5-dimethylpyrazol-1-yl)methane (dmpzm) or bis(4-bromo-3,5-dimethylpyrazol-1-yl)methane (brdmpzm) afford one dimeric complex $[(dmpzm)Cu(\mu\text{-}I)]_2$ and one polymeric complex $[(brdmpzm)Cu(\mu\text{-}I)]_n$, respectively. The formation of different

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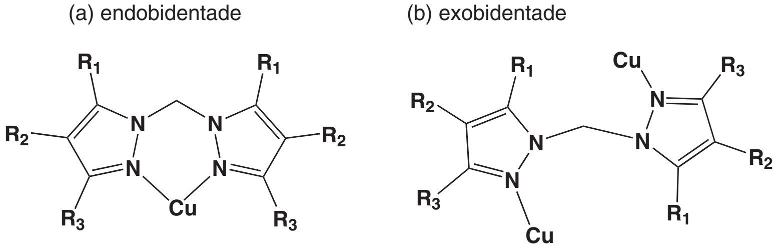


Scheme 1. The two coordination modes of bis(pyrazolyl)methane ligands.

structures showed that the substituents on the pyrazolyl ring may impact structures of the resulting adducts. As shown in scheme 1, bis(pyrazolyl)methane ligands can coordinate to a metal through endo- or exo-bidentate modes. However, each bis(pyrazolyl)methane chelates at one Cu(I) *via* the N,N-bidentate mode. We prepared a new ligand, bis(4-phenyl-pyrazol-1-yl)methane (phpzm), which has phenyl only at 4-positions of the pyrazolyl rings to react with CuX (X = Br, SCN, CN). Two 2-D polymeric complexes, $[Cu(\mu\text{-}Br)(\mu\text{-}phpzm)]_n$ (**1**) and $[\{Cu(\mu\text{-}SCN)\}_2(\mu\text{-}phpzm)]_n$ (**2**), and one 1-D polymeric complex, $[(phpzm)Cu(\mu\text{-}CN)]_n$ (**3**) were isolated. In **1** and **2**, each phpzm is a bridging ligand *via* $\mu\text{-}\eta^1(N)\text{-}\eta^1(N)$ coordination (scheme 1b) while that in **3** chelates to Cu through N,N-bidentate (scheme 1a). Herein, we report syntheses and crystal structures along with luminescent properties.

2. Experimental

2.1. *Materials and instruments*

All solvents were pre-dried over activated molecular sieves and refluxed over the appropriate drying agents under argon. 4-Phenylpyrazole was prepared according to published procedure [26]. Other chemicals and reagents were obtained from commercial sources and used as received. ^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian UNITYplus-300 spectrometer. ^1H and ^{13}C NMR chemical shifts are referenced to the solvent signal in $CDCl_3$. IR spectra were recorded on an FTIR-1000 spectrophotometer as KBr discs (4000–400 cm^{-1}). Elemental analyses for C, H, and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. Emission and excitation spectra were performed on a Varian CARY Eclipse fluorescence spectrophotometer.

2.2. *Preparation of phpzm*

A mixture containing 4-phenylpyrazole (2.89 g, 0.02 mol), KOH (4.48 g, 0.08 mol), K_2CO_3 (10.88 g, 0.08 mol), and benzyltriethylammonium chloride (0.3 g) in CH_2Cl_2 (200 mL) was heated under reflux for 5 h and then cooled to ambient temperature. After filtration, the filtrate was concentrated *in vacuo* to dryness. The white residue was dissolved in water and extracted with $CHCl_3$ (2 × 100 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The resulting white solid was recrystallized from $CHCl_3$ to give white crystals of phpzm, which were collected by filtration and dried *in vacuo*. Yield: 2.61 g (87%); m.p. 209.5–210.5°C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.92 (s, 2H), 7.84 (s, 2H), 7.47 (m, 4H), 7.35 (m, 4H), 7.23 (m, 2H), 6.33 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ 138.6, 131.9, 129.0, 127.0, 126.5, 125.9, 124.9, 66.0. Anal. HRMS (EI) *m*/*z*: Calcd for $C_{19}H_{16}N_4$ 300.1368. Found: 300.1369. Calcd for $C_{19}H_{16}N_4$ (%): C, 75.98; H, 5.37; N, 16.65. Found: C, 76.14; H, 5.77; N, 16.91. IR (KBr disc, cm^{-1}): 3105(w), 3035(w), 3007(w), 1604(m), 1564(m), 1456(m), 1418(s), 1364(m), 1220(m), 1192(m), 1070(m), 1011(m), 950(m), 864(m), 816(w), 767(m), 694(m), 505(w), 458(w).

2.3. *Preparation of 1–3*

2.3.1. Preparation of [Cu(μ-Br)(μ-phpzm)]$_n$ (1). To a Pyrex glass tube (15 cm in length, 7 mm in inner diameter) were added CuBr (15 mg, 0.1 mmol), phpzm (30 mg, 0.1 mmol), and 2 mL of MeCN. The tube was sealed and heated in an oven at 120°C for 1 day and then cooled to room temperature at 5°C/100 min to form colorless crystals of **1**, which were collected by filtration, washed with MeCN and Et_2O, and dried *in vacuo*. Yield: 40 mg (91% based on Cu). Anal. Calcd for $C_{19}H_{16}BrCuN_4$ (%): C, 51.42; H, 3.63; N, 12.62. Found: C, 51.85; H, 3.23; N, 12.89. IR (KBr disc, cm^{-1}): 3066(w), 2999(w), 1611(w), 1572(w), 1448(w), 1417(m), 1397(m), 1367(m), 1215(m), 1191(m), 1182(m), 1077(m), 1018(m), 956(m), 841(s), 749(s), 687(s), 512(m), 456(w).

2.3.2. Preparation of [{Cu(μ-SCN)}$_2$(μ-phpzm)]$_n$ (2). Compound **2** was prepared as colorless crystals in a similar manner to that described for **1** using CuSCN (12 mg, 0.1 mmol) and phpzm (30 mg, 0.1 mmol) in DMF (1 mL) and MeCN (1 mL) at 120°C for 2 days. Yield: 17 mg (61% based on Cu). Anal. Calcd for $C_{21}H_{16}Cu_2N_6S_2$ (%): C, 46.40; H, 2.97; N, 15.46. Found: C, 46.13; H, 2.62; N, 15.81. IR (KBr disc, cm^{-1}): 3105(w), 3092(w), 3032(w), 2161(m), 2112(s), 1606(m), 1565(m), 1459(m), 1438(s), 1419(m), 1368(m), 1219(m), 1191(m), 1071(m), 1012(m), 952(m), 859(m), 761(s), 755(s), 695(s), 516(w), 458(w).

2.3.3. Preparation of [(phpzm)Cu(μ-CN)]$_n$ (3). Compound **3** was prepared as colorless crystals in a similar manner to that described for **1** using CuCN (9 mg, 0.1 mmol) and phpzm (30 mg, 0.1 mmol) in DMF (1 mL) and MeCN (1 mL) at 120°C for 2 days. Yield: 25 mg (65% based on Cu). Anal. Calcd for $C_{20}H_{16}CuN_5$ (%): C, 61.61; H, 4.14; N, 17.96. Found: C, 61.37; H, 4.59; N, 18.23. IR (KBr disc, cm^{-1}): 3109(w), 3029(w), 2115(s), 1607(m), 1567(m), 1460(m), 1442(s), 1383(m), 1369(m), 1333(w), 1212(m), 1193(m), 1068(w), 996(w), 850(m), 776(m), 755(s), 690(s), 515(w), 458(w).

2.4. *X-ray diffraction crystallography*

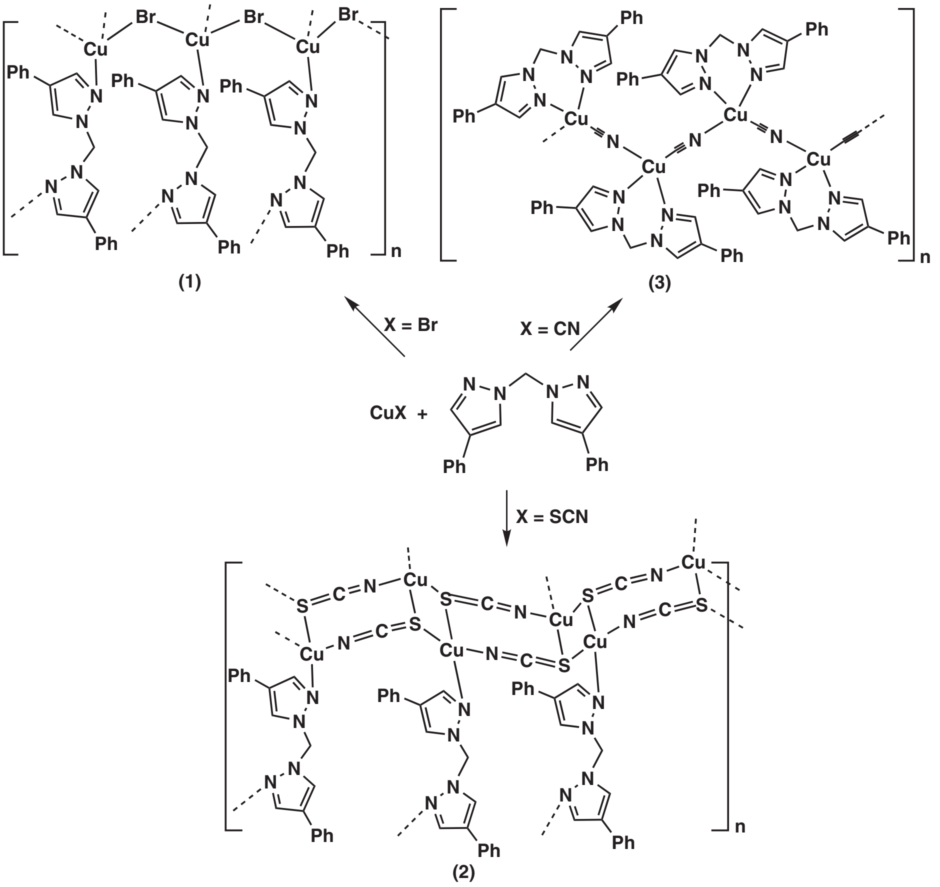
Single crystals of **1**–**3** suitable for X-ray diffraction were obtained directly from the above syntheses. Diffraction intensities of **1**–**3** were collected on a Rigaku Mercury CCD X-ray diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). A colorless block of **1**, a colorless

Table 1. Crystallographic data and structure refinements for **1–3**.

	1	**2**	**3**
Empirical formula	$C_{19}H_{16}BrCuN_4$	$C_{21}H_{16}Cu_2N_6S_2$	$C_{20}H_{16}CuN_5$
Formula weight	443.81	543.60	389.92
Temperature (K)	223(2)	223(2)	193(2)
Wavelength (Å)	0.71075	0.71075	0.71075
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2	*C*2/*c*	*Pnma*
Unit cell dimensions (Å, °)			
a	32.527(12)	22.787(6)	8.856(3)
b	4.0288(14)	5.7298(12)	27.721(10)
c	13.298(5)	18.103(5)	7.189(3)
β	100.311(10)	114.712(6)	
Volume (Å^3), *Z*	1714.5(11), 4	2147.2(9), 4	1764.9(11), 4
Calculated density (Mg m^{-3})	1.719	1.682	1.467
Absorption coefficient (mm^{-1})	3.613	2.197	1.251
F(000)	888	1096	800
Crystal size (mm^3)	$0.32 \times 0.21 \times 0.10$	$0.10 \times 0.50 \times 0.10$	$0.10 \times 0.60 \times 0.18$
θ range for data collection (°)	3.11–27.48	3.7–27.5	3.59–25.50
Limiting indices	$-30 \le h \le 42$; $-5 \le k \le 4$; $-17 \le l \le 14$	$-23 \le h \le 29$; $-7 \le k \le 6$; $-23 \le l \le 17$	$-10 \le h \le 9$; $-30 \le k \le 33$; $-6 \le l \le 8$
Reflections collected	4728	7431	5604
Independent reflection	3214 [*R*(int) = 0.0343]	2442 [*R*(int) = 0.0516]	1626 [*R*(int) = 0.1069]
Completeness to θ (%)	98.0	98.8	96.4
Goodness-of-fit on F^2	1.096	1.098	1.124
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0436$, $wR_2 = 0.0793$	$R_1 = 0.0559$, $wR_2 = 0.0858$	$R_1 = 0.1031$, $wR_2 = 0.2330$
R indices (all data)	$R_1 = 0.0659$, $wR_2 = 0.0858$	$R_1 = 0.0815$, $wR_2 = 0.0947$	$R_1 = 0.1480$, $wR_2 = 0.2601$
Largest difference peak and hole (e Å^{-3})	1.932 and −0.483	0.375 and −0.475	0.865 and −0.786

block of **2**, or a colorless block of **3** was mounted at the top of a glass fiber with grease at 223 K (**1** and **2**) or 193 K (**3**) in a stream of nitrogen. Diffraction data were collected at the ω mode with a detector distance of 35 mm to each crystal. The collected data were reduced by using *CrystalClear* (Rigaku and MSC, Ver. 1.3, 2001) and absorption corrections (multi-scan) were applied, resulting in transmission factors ranging from 0.408 to 0.696 for **1**, from 0.503 to 0.803 for **2**, and from 0.352 to 0.883 for **3**. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1**–**3** were solved by direct methods [27] and refined by full-matrix least-squares on F^2 [27, 28]. Needles of **3** were very small showing weak diffractions, especially at high angles, which made the final *R* value relatively high. All non-hydrogen atoms were refined anisotropically while all hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The final refinement was based on 3214 (**1**), 2442 (**2**), and 1626 (**3**) reflections with $I > 2.00\sigma(I)$ and 228 (**1**), 142 (**2**), and 124 (**3**) variable parameters, and $w = 1/[\sigma^2(F_o^2) + (0.0207P)^2]$ (**1**), $w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 5.2767P]$ (**2**), and $w = 1/[\sigma^2(F_o^2) + (0.1153P)^2 + 3.3602P]$ (**3**) (where $P = (F_o^2 + 2F_c^2)/3$). All calculations were performed on a Dell workstation using the *CrystalStructure* crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). A summary of the important crystallographic information for **1**–**3** is tabulated in table 1.



Scheme 2. Syntheses of **1**–**3**.

3. Results and discussion

3.1. *Preparation and characterization of phpzm and 1–3*

Using a similar synthetic approach to bis(4-benzyl-3,5-dimethyl-1H-pyrazol-1-yl)methane) (bzdmpzm) [24b], 4-phenylpyrazole was allowed to react with KOH, K_2CO_3, and benzyltriethylammonium chloride in CH_2Cl_2 to produce phpzm in 87% yield; phpzm is soluble in CH_2Cl_2, $CHCl_3$, DMSO, and DMF. ^1H NMR spectra of phpzm in $CDCl_3$ at room temperature show one singlet (2H) at $\delta = 6.33$, assigned to two protons of methylene. Singlets at $\delta = 7.92$ and 7.84 ppm were ascribed to four protons of the pyrazolyl ring of phpzm. Multiplets at $\delta = 7.47$, 7.35, and 7.23 ppm were ascribed to the ten protons of phenyls of phpzm. As shown in scheme 2, solvothermal reactions of CuBr and phpzm (molar ratio = 1 : 1) in MeCN at 120°C for 2 days followed by a standard workup afforded **1** in 91% yield. Similar reactions of phpzm with CuSCN or CuCN led to **2** and **3**, respectively. The substituents on the pyrazolyl rings did have a significant influence on the $[CuX]_n$ structure and the coordination modes of bis(pyrazolyl)methane. The 1-D split-stair chain of **1** is similar to those in $\{[CuCl]_2(BBTH)\}_n$ (BBTH = 1,6-bi(benzotriazole)hexane) [29] and [(brdmpzm)Cu(μ-X)]$_n$ (X = Cl, Br, I) [25b], but different from those of dimeric complexes [(L)Cu(μ-I)]$_2$ (L = dmpzm [24a], bzdmpzm [24b]). In **2**, the framework of CuSCN was cleaved into the 1-D staircase-like [CuSCN]$_n$ chains, different from the 1-D single-strand spiral chain in [(dmpzm)Cu(μ-SCN)]$_n$ and the split-stair chain in [(bzdmpzm)Cu(μ-SCN)]$_n$. The 1-D zigzag [Cu(μ-CN)]$_n$ chain in **3** is similar to those of [(dmpzm)Cu(μ-CN)]$_n$ and [(brdmpzm)Cu(μ-CN)]$_n$. In **1** and **2**, phpzm takes μ-$\eta^1:\eta^1$ coordination to link two Cu(I)'s, while each dmpzm, bzdmpzm, brdmpzm, or phpzm in [(dmpzm)Cu(μ-X)]$_n$ (X = I, CN, SCN), [(bzdmpzm)Cu(μ-X)]$_n$ (X = I, SCN), [(brdmpzm)Cu(μ-X)]$_n$ (X = Cl, Br, I, CN) and **3** chelates each Cu. Compounds **1**–**3** are relatively air- and moisture-stable, and insoluble in common solvents such as CH_3OH, $CHCl_3$, MeCN, THF, DMF, and DMSO. The elemental analyses were consistent with the chemical formulae. In IR spectra of **1**–**3**, strong bands at 1572/1448 cm^{-1} (**1**), 1565/1459 cm^{-1} (**2**), and 1567/1460 cm^{-1} (**3**) were assigned as C = N stretching vibrations of phpzm. The strong band at 2161/2112 cm^{-1} (**2**) was assigned to bridging thiocyanate while the strong band at 2115 cm^{-1} (**3**) was assigned to bridging C≡N stretch. The identities of **1**–**3** were finally confirmed by X-ray crystallography.

3.2. *Descriptions of structures of 1–3*

3.2.1. [Cu(μ-Br)(μ-phpzm)]$_n$ (1). Crystallizing in the monoclinic space group *C*2, the asymmetric unit for **1** consists of one discrete [CuBr(phpzm)]. Complex **1** contains a 2-D layer structure in which 1-D split-stair [CuBr]$_n$ chains are interlinked by phpzm bridges (figure 1). The 1-D array of Cu(I) are connected through a set of doubly bridging Br$^-$'s. Such a 1-D [Cu(μ-Br)]$_n$ chain is similar to those observed in other 1-D polymers [(brdmpzm)Cu(μ-X)]$_n$ (X = Cl, Br, I) [25b]. Each phpzm links two Cu(I)'s through μ-$\eta^1:\eta^1$-N,N coordination, which is different from the chelating coordination observed in [(brdmpzm)Cu(μ-X)]$_n$ (X = Cl, Br, I) [25b] and [(L)Cu(μ-I)]$_2$ (L = dmpzm [24a], bzdmpzm [24b]). Each Cu is coordinated by two bromides and two nitrogen atoms from two phpzm to form a distorted tetrahedral coordination geometry. In **1**, the mean Cu–N bond length (2.055(8) Å) (table 2) is slightly shorter than those of [(brdmpzm)Cu(μ-X)]$_n$ (2.077(8) Å for X = Cl; 2.074(8) Å for X = Br; 2.095(5) Å for X = I) [25b]. The mean Cu-μ-Br bond length (2.484(2) Å) in **1** is somewhat longer than that in [(brdmpzm)Cu(μ-Br)]$_n$ (2.448(3) Å) [24a]. The N(1)–Cu(1)–N(3) angle (101.40(17)°) in **1** is much larger than the N–Cu–N bite angles in [(brdmpzm)Cu(μ-X)]$_n$ (92.2(5)° for X = Cl; 92.9(5)° for X = Br; 92.3(3)° for X = I), [(bzdmpzm)Cu(μ-I)]$_2$ (92.85(14)°) [24b], and [(dmpzm)Cu(μ-I)]$_2$ (91.12(15)°) [24a]. The Cu–Br–Cu bond angle (108.38(4)°) in **1** is smaller than that in [(brdmpzm)Cu(μ-Br)]$_n$ (113.76(11)°) [25b]. The N(2)–C(10)–N(2C) and N(4)–C(20)–N(4D) angles are 111.9(7)° and 113.5(7)°, respectively, similar to that observed in [Cu(μ-Br)(brdmpzm)]$_n$ (112.1(12)° [25b]. The N(2)–C(10) and N(4)–C(20) bond distances are 1.461(7) Å and 1.459(6) Å, respectively. Their mean length (1.460 Å) is longer than the corresponding ones in [Cu(μ-I)(dmpzm)]$_2$ (1.444(6) Å) [24a] and [Cu(μ-X)(brdmpzm)]$_n$ (1.447(10) Å (X = Cl), 1.434(12) Å (X = Br), 1.444(7) Å (X = I)) [25b]. The dihedral angles between two pyrazolyls of phpzm in **1** are 64.9° and 58.7°, slightly larger than the ones between two pyrazolyl groups at the same chelate site in [$\{Cu_2X_2(tdmpp)\}$]$_n$ (56.99° (X = Cl)

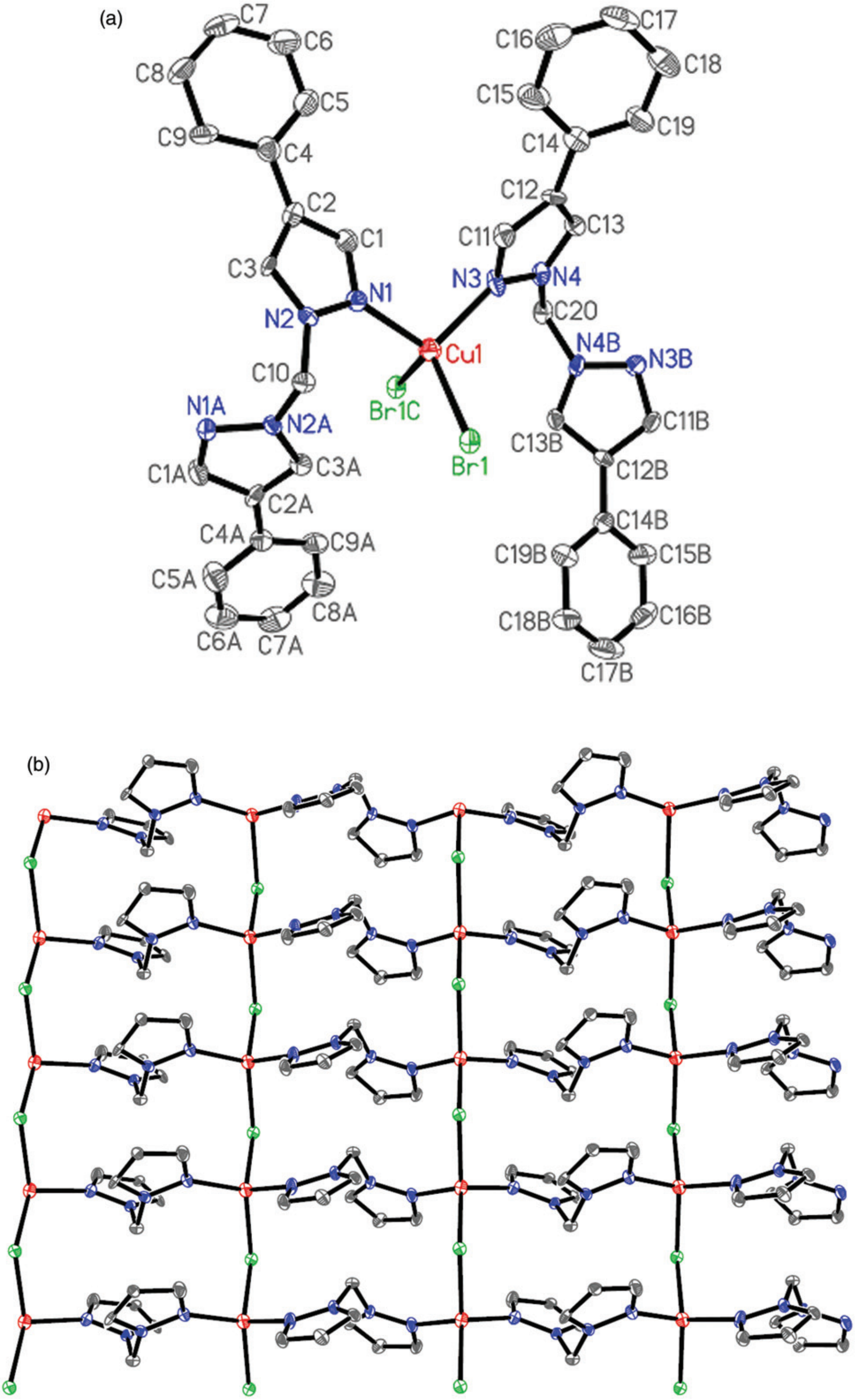


Figure 1. (a) View of the coordination geometry of each Cu(I) in **1** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Symmetry codes: A: x, $1+y$, z; B: x, $1-y$, z; C: $3/2+x$, $1/2+y$, $1+z$. (b) View of the 2-D layer structure of **1** extending along the *bc*-plane.

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Cu(1)–N(1)	2.057(4)	Cu(1)–N(3)	2.053(4)
Cu(1)–Br(1)	2.4773(17)	Cu(1)–Br(1A)	2.4907(17)
N(2)–C(10)	1.461(7)	N(4)–C(20)	1.459(6)
N(1)–Cu(1)–N(3)	101.40(17)	N(3)–Cu(1)–Br(1)	110.3(3)
N(1)–Cu(1)–Br(1)	115.3(2)	N(3)–Cu(1)–Br(1A)	113.6(3)
N(1)–Cu(1)–Br(1A)	107.9(2)	Br(1)–Cu(1)–Br(1A)	108.38(4)
N(2)–C(10)–N(2C)	111.9(7)	N(4)–C(20)–N(4D)	113.5(7)
Cu(1)–Br(1)–Cu(1B)	108.38(4)		

Symmetry codes: A: x, $1+y$, z; B: x, $1-y$, z; C: $3/2+x$, $1/2+y$, $1+z$; D: $3/2+x$, $1/2+y$, z.

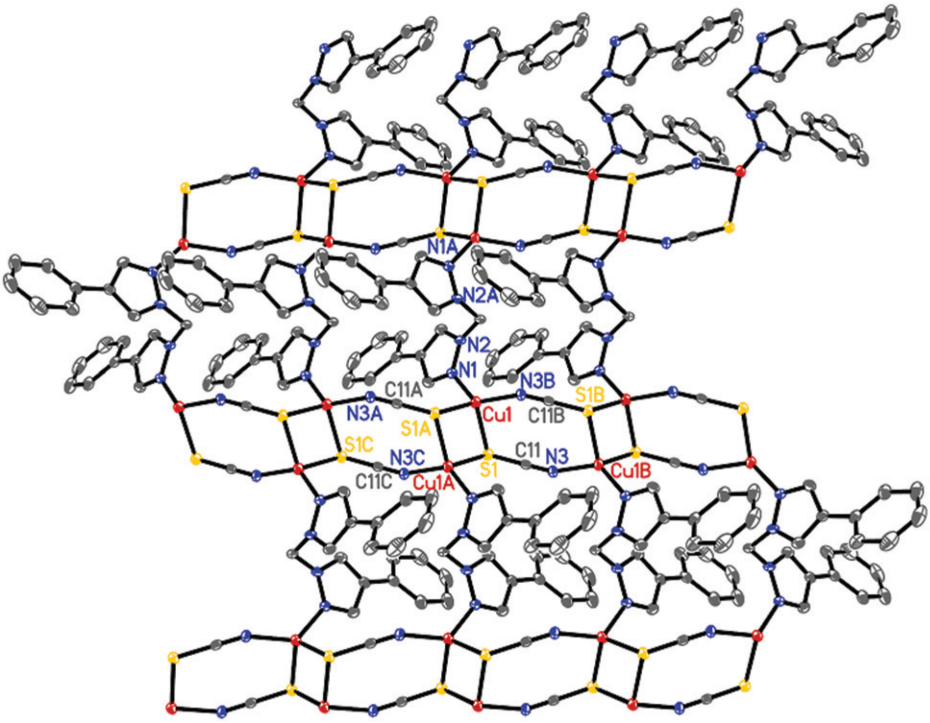


Figure 2. View of the 2-D network of **2** extending along the *bc*-plane. All hydrogen atoms were omitted for clarity. Symmetry codes: A: $1-x$, y, $1/2-z$; B: $1-x$, $1+y$, $1/2-z$; C: $3/2+x$, $1/2+y$, $1+z$.

to 54.08° (X = Br) to 52.00° (X = I)), but much smaller than those between two adjacent $[CuX]_2$ cores in $[\{Cu_2X_2(tdmpp)\}]_n$ (84.97° (X = Cl) to 86.39° (X = Br) to 86.42° (X = I)) [11b].

3.2.2. $[\{Cu(\mu\text{-}SCN)\}_2(\mu\text{-}phpzm)]_n$ (2). Complex **2** crystallizes in the monoclinic space group *C*2/*c* and with an asymmetric unit that contains half a $[\{Cu(NCS)\}_2(phpzm)]$. Complex **2** is another 2-D layer network (extended along the *bc*-plane) in which 1-D staircase $[CuSCN]_n$ chains (parallel to the *b*-axis) are interlinked by phpzm bridges (figure 2). Each $[CuSCN]_n$ chain is assembled from linking each eight-membered Cu–NCS–Cu–NCS ring *via* four Cu–S(SCN) bonds. Such a 1-D staircase $[CuSCN]_n$

Table 3. Selected bond lengths (Å) and angles (°) of **2**.

Cu(1)–N(1)	1.993(3)	Cu(1)–S(1)	2.5272(14)
Cu(1)–N(3A)	1.943(3)	Cu(1)–S(1B)	2.3753(11)
N(3)–Cu(1A)	1.943(3)	S(1)–Cu(1B)	2.3753(11)
S(1)–C(11)	1.654(4)	N(3)–C(11)	1.158(4)
N(2)–C(10)	1.439(4)	Cu(1)···Cu(1B)	2.7005(12)
N(2)–C(10)–N(2C)	110.3(4)	N(3)–C(11)–S(1)	178.6(4)
N(3A)–Cu(1)–N(1)	128.65(13)	N(3A)–Cu(1)–S(1B)	105.16(10)
N(1)–Cu(1)–S(1B)	107.96(9)	N(3A)–Cu(1)–S(1)	102.01(10)
N(1)–Cu(1)–S(1)	99.61(10)	S(1B)–Cu(1)–S(1)	113.23(4)
C(11)–S(1)–Cu(1B)	102.18(13)	C(11)–S(1)–Cu(1)	96.44(14)
C(11)–N(3)–Cu(1)	158.4(3)		

Symmetry codes: A: $1-x$, y, $1/2-z$; B: $1-x$, $1+y$, $1/2-z$; C: $3/2+x$, $1/2+y$, $1+z$.

chain is different from the 1-D single-strand spiral chain in [(dmpzm)Cu(μ-NCS)]$_n$ [25a] and the 1-D zigzag chain of [(bzdmpzm)Cu(μ-NCS)]$_2$ [24b], which may be due to the steric hindrance among the different substituents on the pyrazolyl rings of dmpzm, bzdmpzm, or phpzm. In **2**, each thiocyanate is almost linear with N(3)–C(11)–S(1) bond angle of 178.6(4)° (table 3), comparable to those of the corresponding ones of [(dmpzm)Cu(μ-NCS)]$_n$ (178.9(6)°) and [(bzdmpzm)Cu(μ-NCS)]$_n$ (178.7(2)°). Each phpzm is μ-$\eta^1:\eta^1$-N,N coordination. Each Cu in **2** is tetrahedrally coordinated by one nitrogen atom from phpzm, one nitrogen atom from μ-NCS and two sulfur atoms from another two μ-NCS$^-$. The Cu(1)–S(1) bond length (2.3753(11) Å) is slightly shorter than those found in [(dmpzm)Cu(μ-NCS)]$_n$ (2.3813(6) Å) and [(bzdmpzm)Cu(μ-NCS)]$_n$ (2.386(19) Å), but longer than that of [{Cu(μ-SCN)}$_2$(tdmpp)]$_n$ (2.3485(9) Å; tdmpp = 1,1,3,3-tetrakis(3,5-dimethyl-1-pyrazole)propane) [11b]. The Cu–N(phpzm) bond length (1.993(3) Å) is shorter than those in [(bzdmpzm)Cu(μ-NCS)]$_n$ (2.102(4) Å) [24b], [Cu$_2$(μ-dppm)$_2$(μ-HL)](NO$_3$)$_2$ (2.12 Å; HL = 3,5-bis{6(2,2′-dipyridyl)}pyrazole; dppm = bis(diphenylphosphino)methane) [6b] and [(dmpzm)Cu(μ-NCS)]$_n$ (2.0823(17) Å) [25a]. The Cu–N(NCS) length (1.943(3) Å) is longer than those found in [(bzdmpzm)Cu(μ-NCS)]$_n$ (1.937(5) Å) and [(dmpzm)Cu(μ-NCS)]$_n$ (1.9382(19) Å), but shorter than that of [{Cu(μ-SCN)}$_2$(tdmpp)]$_n$ (1.9670(2) Å). The Cu(1)···Cu(1A) contact (2.7005(12) Å) is comparable to that in [(bzdmpzm)Cu(μ-I)]$_2$ (2.7056(14) Å) [24b], but slightly shorter than that in [(dmpzm)Cu(μ-I)]$_n$ (2.7412(13) Å) [24a]. The N(2)–C(10) bond length of 1.439(4) Å is shorter than that in **1**. The S(1)–C(11) and N(3)–C(11) bond distances are 1.654(4) Å and 1.158(4) Å, close to the corresponding ones in [(dmpzm)Cu(μ-NCS)]$_n$ (1.656(2) Å, 1.155(3) Å) [24b]. In **2**, the dihedral angle between two pyrazolyl groups of phpzm of 81.5° is much larger than the corresponding one in **1**.

3.2.3. [(phpzm)Cu(μ-CN)]$_n$ (3). Compound **3** crystallizes in the orthorhombic space group *Pnma* and its asymmetric unit contains a discrete [CuCN(phpzm)] molecule. In **3**, each Cu(I) ion is connected to adjacent Cu(I) by CN$^-$, forming a 1-D chain extended along the *a*-axis. Compound **3** consists of a 1-D zigzag [Cu(μ-CN)]$_n$ chain, in which each Cu is chelated by one phpzm (figure 3). This chain is similar to those found in [(dmpzm)Cu(μ-CN)]$_n$ [25a] and [(brdmpzm)Cu(μ-CN)]$_n$ [25b]. However, the C(11)–N(3)–Cu(1) bond angle (179.5(9)°) (table 4) is somewhat larger than those observed in [(dmpzm)Cu(μ-CN)]$_n$ (175.5(3)°) [25a] and [{(brdmpzm)Cu}(μ-CN)]$_n$ (159.7(6)°) [25b].

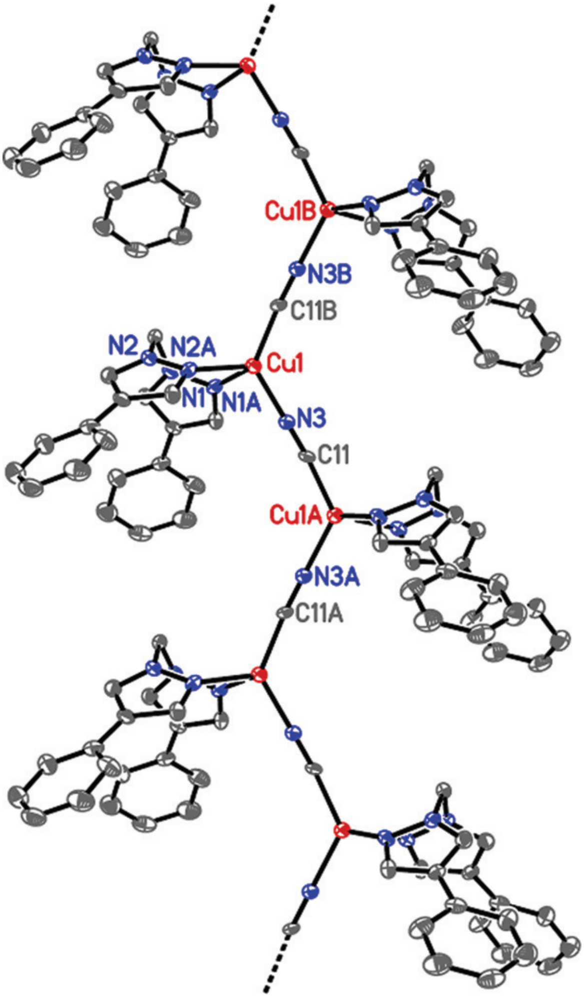


Figure 3. View of a section of the 1-D chain of **3** extending along the *c*-axis. All hydrogen atoms are omitted for clarity. Symmetry codes: A: x, $1/2-y$, $-1/2+z$; B: $1/2-x$, $-1/2+y$, $-1/2+z$.

The N(3)–C(11)–Cu(1A) bond angle (175.2(10)°) is smaller than those of $[(\text{brdmpzm})\text{Cu}(\mu\text{-CN})]_n$ (179.9(7)°) [25b] and $[(\text{dmpzm})\text{Cu}(\mu\text{-CN})]_n$ (177.1(5)°) [25a]. These differences may be due to the different groups on the pyrazolyl rings of dmpzm, brdmpzm, and phpzm. Each Cu in **3** takes distorted tetrahedral coordination with N(3) and C(11B) from two bridging CN^- groups, and N(1) and N(1A) from the same phpzm. The N(1)–Cu(1)–N(1A) bite angle (88.5(4)°) is comparable to that observed in $[(\text{dmpzm})\text{Cu}(\mu\text{-CN})]_n$ (88.84(7)°) [25a], but smaller than that in $[(\text{brdmpzm})\text{Cu}(\mu\text{-CN})]_n$ (89.6(2)°) [25b]. The Cu–N(phpzm) bond length (2.159(7) Å) is longer than that in $\{[\text{CuCl}]_2(\text{BBTH})\}_n$ (2.073 Å) [29], but close to those of $[(\text{brdmpzm})\text{Cu}(\mu\text{-CN})]_n$ (2.116(4) Å) [25b] and $[(\text{dmpzm})\text{Cu}(\mu\text{-CN})]_n$ (2.168(2) Å) [25a]. The Cu–N(CN) bond distance (1.924(9) Å) is shorter than that in $[(\text{brdmpzm})\text{Cu}(\mu\text{-CN})]_n$ (2.030(7) Å) [25b]. The $\text{C}\equiv\text{N}$ distance (1.162(14) Å) is close to those of $[(\text{brdmpzm})\text{Cu}(\mu\text{-CN})]_n$

Table 4. Selected bond lengths (Å) and angles (°) of **3**.

Cu(1)–N(1)	2.159(7)	Cu(1)–N(3)	1.924(9)
Cu(1)–N(1A)	2.159(7)	Cu(1)–C(11B)	1.895(11)
N(2)–C(10)	1.440(9)	N(3)–C(11)	1.162(14)
C(11B)–Cu(1)–N(3)	126.8(4)	C(11B)–Cu(1)–N(1A)	113.8(3)
N(3)–Cu(1)–N(1A)	103.4(2)	C(11B)–Cu(1)–N(1)	113.8(3)
N(3)–Cu(1)–N(1)	103.4(2)	N(1A)–Cu(1)–N(1)	88.5(4)
C(11)–N(3)–Cu(1)	179.5(9)	N(3)–C(11)–Cu(1C)	175.2(10)

Symmetry codes: A: $+x$, $1/2-y$, $-1/2+z$; B: $1/2-x$, $-1/2+y$, $-1/2+z$; C: $-1/2-x$, $-1/2+y$, $-1/2+z$.

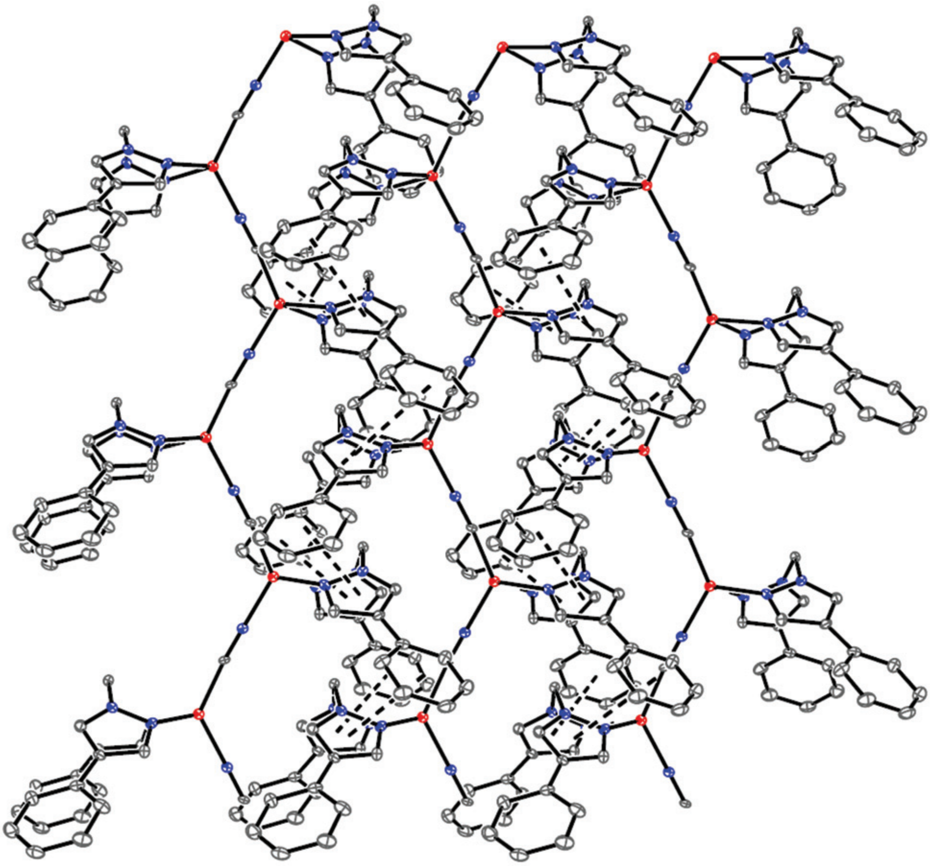


Figure 4. View of the 2-D layer structure (extending along the *ac*-plane) formed by π–π interactions among the pyrazolyl rings and phenyls of phpzm in **3**.

(1.162(11) Å) [25b] and $[(dmpzm)Cu(\mu\text{-}CN)]_n$ (1.156(4) Å) [25a]. The N(2)–C(10) bond length is 1.440(9) Å, comparable to the one in **2** (1.439(4) Å), but slightly shorter than that in **1** (1.460 Å). The dihedral angle between two pyrazolyl groups of phpzm in **3** of 83.3° is much larger than the corresponding ones in $[\{Cu_2X_2(tdmpp)\}]_n$ (56.99° (X = Cl) to 54.08° (X = Br) to 52.00° (X = I) [11b]. Two pyrazolyl rings of each phpzm produce

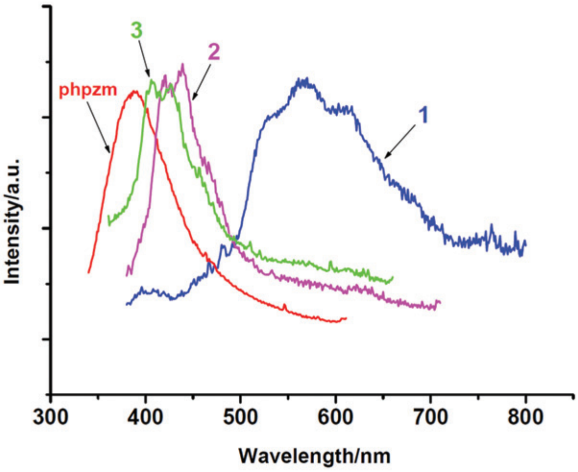


Figure 5. Emission spectra of phpzm and **1**–**3** in the solid state at ambient temperature.

π–π interactions (3.867 Å) with the phenyl groups of the neighboring chains, which leads to the formation of a 2-D layer structure extending along the *ac*-plane (figure 4).

3.3. *Luminescent properties of 1–3*

Photoluminescent properties of **1**–**3** along with phpzm in the solid state at room temperature were studied (figure 5). Upon excitation at 316 nm, phpzm exhibited photoluminescence with an emission maximum at 388 nm, while dmpzm and bzdmpzm exhibit photoluminescence with emission maxima at 562 nm ($\lambda_{ex} = 397$ nm, dmpzm) and 297 nm ($\lambda_{ex} = 250$ nm, bzdmpzm). The brdmpzm did not show luminescence at room temperature. The different luminescence properties of these bis(pyrazolyl)methanes may be due to the different substituents on pyrazolyl. Upon excitation at 323 nm (**1**), 360 nm (**2**), or 350 nm (**3**), **1**–**3** exhibit photoluminescence with emission maxima at 565 nm (**1**), 439 nm (**2**), and 425 nm (**3**). Emission maxima of **1**–**3** are red-shifted compared to that of phpzm, which may be due to the electron-withdrawing properties of bromide, thiocyanate, and cyanide. Compared with bromide in **1** and thiocyanate in **2**, cyanide in **3** is the strongest electron-withdrawing group and the weakest electron donor, producing the largest transition energy and thus exhibits the shortest λ_{max}^{em} at 425 nm. Complex **1** showed its emission band at longer wavelength than those of **2** and **3**, which may be due to the fact that bromide has weaker electron-withdrawing ability than thiocyanide and cyanide and the different $[Cu_nX_n]$ structural motifs and resulting structures. The emissions of **1**–**3** may be attributed to bromide, thiocyanate, or cyanide to phpzm ligand charge transfer (XLCT) [11b]. Compared to $[(brdmpzm)Cu(\mu\text{-Br})]_n$ ($\lambda_{max}^{em} = 462$ nm) [25b], **1** exhibited lower energy transition, which may originate from the different substituents on the pyrazolyl rings. Relative to that of $[(dmpzm)Cu(\mu\text{-SCN})]_n$ ($\lambda_{max}^{em} = 578$ nm) [25a] or $[CuCN(brdmpzm)]_n$ (($\lambda_{max}^{em} = 480$ nm [25b]), **2** or **3** exhibits a blue-shifted emission band ($\lambda_{max} = 439$ nm or 425 nm).

4. Conclusion

We demonstrated that reactions of CuX (X = Br, SCN or CN) with equimolar phpzm under solvothermal conditions produced two 2-D coordination polymers **1** and **2** and one 1-D polymer **3**. In **1**, 1-D zigzag $[\mathrm{Cu}(\mu\text{-Br})]_n$ chains are bridged by phpzm to form a 2-D network. Compound **2** possesses $[\mathrm{Cu}(\mu\text{-SCN})]_n$ double chains connected by phpzm to form another 2-D network, while **3** exhibits a 1-D zigzag chain built of $[\mathrm{CuCN}]_n$ chain with each phpzm chelated at one Cu(I). The substituent on the pyrazolyl rings of the poly(pyrazolyl)methanes affects the coordination of ligands, the $[\mathrm{CuX}]_n$ structural motifs, the final structures, and luminescent properties of Cu(I) halide and pseudohalide complexes of bis(pyrazolyl)methane ligands. If the pyrazolyl rings of poly(pyrazolyl)methanes are modified by nitrogen-containing heterocycle or carboxylic groups [5b, 6b, 8b], these ligands can coordinate through more coordination modes, which may result in a series of coordination compounds with more interesting topological structures and properties. Studies on these aspects are underway in our laboratory.

Supplementary material

CCDC nos 840510 (**1**), 840511 (**2**), and 840512 (**3**) contain the supplementary crystallographic data. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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References

[1] (a) S. Trofimenko. *J. Am. Chem. Soc.*, **88**, 1842 (1966); (b) S. Trofimenko. *J. Am. Chem. Soc.*, **92**, 5118 (1970).
[2] (a) R. Czerwieniec, J.B. Yu, H. Yersin. *Inorg. Chem.*, **50**, 8293 (2011); (b) W.L. Leong, J.J. Vittal. *Chem. Rev.*, **111**, 688 (2011); (c) S.T. Meek, J.A. Greathouse, M.D. Allendorf. *Adv. Mater.*, **23**, 249 (2011);

(d) A.M. Kirillov. *Coord. Chem. Rev.*, **255**, 1603 (2011); (e) C. Janiak, J.K. Vieth. *New J. Chem.*, **34**, 2366 (2010); (f) K.M. Fromm, J.L. Sagué, L. Mirolo. *Macromol. Symp.*, **291–292**, 75 (2010).

[3] S. Kealey, P.W. Miller, N.J. Long, C. Plisson, L. Martarello, A.D. Gee. *Chem. Commun.*, 3696 (2009).

[4] W. Kaim, C. Titze, T. Schurr, M. Sieger, M. Lawson, J. Jordanov, D. Rojas, A.M. García, J. Manzur. *Z. Anorg. Allg. Chem.*, **631**, 2568 (2005).

[5] (a) K. Fujisawa, T. Ono, Y. Ishikawa, N. Amir, Y. Miyashita, K.I. Okamoto, N. Lehnert. *Inorg. Chem.*, **45**, 1698 (2006); (b) X.F. Feng, C. Yang, Z.W. Liao, Y.M. Song, H.X. Huang, G.M. Sun, M.B. Luo, S.J. Liu, F. Luo. *J. Coord. Chem.*, **65**, 104 (2012).

[6] (a) J.M. Munñoz-Molina, A. Caballero, M.M. Díaz-Requejo, S. Trofimenko, T.R. Belderraín, P.J. Párez. *Inorg. Chem.*, **46**, 7725 (2007); (b) J.L. Chen, W. Gua, X.F. Cao, H.R. Wen, R.J. Hong. *J. Coord. Chem.*, **64**, 1903 (2011).

[7] N. Kitajima, K. Fujisawa, M. Tanaka, Y. Moro-oka. *J. Am. Chem. Soc.*, **114**, 9232 (1992).

[8] (a) K. Fujisawa, A. Tateda, Y. Miyashita, K.i. Okamoto, F. Paulat, V.K.K. Praneeth, A. Merkle, N. Lehnert. *J. Am. Chem. Soc.*, **130**, 1205 (2008); (b) F.L. Hu, X.H. Yin, J. Lu, Y. Mi, J.C. Zhuang, W.Q. Luo. *J. Coord. Chem.*, **63**, 263 (2010).

[9] I. Krummenacher, H. Rüegger, F. Breher. *Dalton Trans.*, 1073 (2006).

[10] Y.J. Huang, Y.L. Song, Y. Chen, H.X. Li, Y. Zhang, J.P. Lang. *Dalton Trans.*, 1411 (2009).

[11] (a) L.L. Li, L.L. Liu, A.X. Zheng, Y.J. Chang, M. Dai, Z.G. Ren, H.X. Li, J.P. Lang. *Dalton Trans.*, **39**, 7659 (2010); (b) L. Zhang, Z.G. Ren, H.X. Li, J.P. Lang. *CrystEngComm*, **13**, 1400 (2011).

[12] T.N. Sorrell, A.S. Borovik. *Inorg. Chem.*, **26**, 1957 (1987).

[13] M. Kujime, T. Kurahashi, M. Tomura, H. Fujii. *Inorg. Chem.*, **46**, 541 (2007).

[14] M.M. Kimani, J.L. Brumaghim, D. VanDerveer. *Inorg. Chem.*, **49**, 9200 (2010).

[15] B.R. Manzano, F.A. Jalón, I.M. Ortiz, M.L. Soriano, F.G. de la Torre, J. Elguero, M.A. Maestro, K. Mereiter, T.D.W. Claridge. *Inorg. Chem.*, **47**, 413 (2008).

[16] R. Wanke, P. Smoleński, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, A.J.L. Pombeiro. *Inorg. Chem.*, **47**, 10158 (2008).

[17] A.T. Baker, D.C. Craig, G. Dong. *Inorg. Chem.*, **35**, 1091 (1996).

[18] M.I. Ortiz, M.L. Soriano, M.P. Carranza, F.A. Jalón, J.W. Steed, K. Mereiter, A.M. Rodríguez, D. Quiñonero, P.M. Deyà, B.R. Manzano. *Inorg. Chem.*, **49**, 8828 (2010).

[19] K. Fujisawa, Y. Noguchi, Y. Miyashita, K.-i. Okamoto, N. Lehnert. *Inorg. Chem.*, **46**, 10607 (2007).

[20] M. Kujime, C. Izumi, M. Tomura, M. Hada, H. Fujii. *J. Am. Chem. Soc.*, **130**, 6088 (2008).

[21] (a) G. Pampaloni, R. Peloso, D. Belletti, C. Graiff, A. Tiripicchio. *Organometallics*, **26**, 4278 (2007); (b) D.L. Reger, J.E. Collins, A.L. Rheingold, L.M. Liable-Sands. *Organometallics*, **15**, 2029 (1996).

[22] N. Zhao, J.C. Bullinger, M.J. Van Stipdonk, C.L. Stern, D.M. Eichhorn. *Inorg. Chem.*, **47**, 5945 (2008).

[23] (a) L. Zhang, M. Du, L. Tong, X. Leng, Z. Wang. *Acta Crystallogr.*, **C56**, 1210 (2000); (b) F. Bonati, A. Cingolani, G.G. Lobbia, D. Leonesi, A. Lorenzotti, C. Pettinari. *Gazz. Chim. Ital.*, **120**, 341 (1990); (c) C. Pettinari, F. Marchetti, R. Polimante, A. Cingolani, G. Portalone, M. Colapietro. *Inorg. Chim. Acta*, **249**, 215 (1996); (d) M.J. Calhorda, P.J. Costa, O. Crespo, M. Concepción Gimeno, P.G. Jones, A. Laguna, M. Naranjo, S. Quintal, Y.J. Shi, M. Dolores Villacampa. *Dalton Trans.*, 4104 (2006).

[24] (a) Y. Xu, H.X. Li, W.H. Zhang, Y. Zhang, J.P. Lang. *Acta Cryst.*, **C61**, m4 (2005); (b) H.H. Wang, H.X. Li, Z.G. Ren, Y. Chen, J.P. Lang. *Chin. J. Chem.*, **28**, 1373 (2010); (c) K. Fujisawa, Y. Noguchi, Y. Miyashita, K.-i. Okamoto, N. Lehnert. *Inorg. Chem.*, **46**, 10607 (2007); (d) A. Boni, G. Pampaloni, R. Peloso, D. Belletti, C. Graiff, A. Tiripicchio. *J. Organomet. Chem.*, **691**, 5602 (2006).

[25] (a) Y. Xu, Z.G. Ren, H.X. Li, W.H. Zhang, J.X. Chen, Y. Zhang, J.P. Lang. *J. Mol. Struct.*, **782**, 150 (2006); (b) H.Y. Li, Y. Zhang, Y.C. Ding, M. Wang, L.X. Dai, J.P. Lang. *J. Mol. Struct.*, **996**, 90 (2011); (c) J. Xia, Z.J. Zhang, W. Shi, J.F. Wei, P. Cheng. *Cryst. Growth Des.*, **10**, 2323 (2010).

[26] D.L. Reger, J.R. Gardinier, T.C. Grattan, M.R. Smith, M.D. Smith. *New J. Chem.*, **27**, 1670 (2003).

[27] G.M. Sheldrick. *SHELXS-97*, *Program for Solution of Crystal Structures*, University of Göttingen, Germany (1997).

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

[29] X. Gao, Q.G. Zhai, X.J. Dui, S.N. Li, Y.C. Jiang, M.C. Hu. *J. Coord. Chem.*, **63**, 214 (2010).