

Electronic Supplementary Information

for

Hydrogen and Halogen Bond Mediated Coordination Polymers of Chloro-substituted Pyrazin-2-amine Copper(I) Bromide Complexes

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- 1. Materials and methods.** The solvents acetone (Ace), chloroform (CHCl₃), dichloromethane (DCM), ethanol (EtOH) and acetonitrile (MeCN) were of at least reagent grade and used as received. The following reagents were purchased commercially and used as received: 2,3-dichloropyrazine, 2,6-dichloropyrazine, 2-amino-5-chloropyrazine (**2**), N-chlorosuccinimide, aqueous ammonium hydroxide (28-30 %) solution and Cupric bromide (CuBr₂). The chemicals 2-amino-3-chloropyrazine (**1**)¹, 2-amino-6-chloropyrazine (**3**)² and 2-amino-3,5-dichloropyrazine (**4**)³ were prepared according to literature procedures. The following reagents were prepared and purified according to a modified literature procedure⁴ : 2-amino-3,6-dichloropyrazine (**5**), 2-amino-5,6-dichloropyrazine (**6**) and 2-amino-3,5,6-trichloropyrazine (**7**) as described below. All reactions were performed in air, unless otherwise stated, and the isolated crystals were collected by filtration on a 10 mm medium sintered Pyrex Buchner funnel and air dried for several days before characterization by IR and X-ray diffraction studies. Thin layer chromatography (TLC) were performed on a silica gel matrix on aluminum plates using DCM as eluent spots were illuminated under 256 nm UV lamp. Column (flash) chromatography were performed on Kieselgel 60 (0.040-0.063 mm) with a column of approx. 3 cm O.D. x 50 cm in length using DCM as solvent and eluant.

- 2. Preparation of 2-amino-3,6-dichloropyrazine (5), 2-amino-5,6-dichloropyrazine (6) and 2-amino-3,5,6-trichloropyrazine (7) by a one-pot synthesis route:** To a solution of 2-amino-6-chloropyrazine (**2**; 2.202 g, 16.998 mmol) in 50 mL of CHCl_3 was added solid N-chlorosuccinimide (4.535 g, 33.962 mmol) in one portion. The mixture was refluxed for 1.5 h to afford an orange solution, cooled to rt and then the solvent removed under reduced pressure. The solid was treated with 50 mL of a hot aqueous solution of 5 % sodium bisulfate and the white insoluble collected by filtration, washed with water and then allowed to air dry for 12 h. The TLC indicated four well separated spots and the crude product (2.940 g) was purified by flash column chromatography leading to three components being eluted from the column:
- 2-amino-3,5,6-trichloropyrazine (7):** R_f (DCM) = 0.68; Recrystallized from cyclohexane as clear, colorless needles. Collected 1.237 g, 37 % yield based on **2**. $^1\text{H-NMR}$ (CDCl_3): δ 5.09 br, s (NH_2).
 - 2-amino-3,6-dichloropyrazine (5):** R_f (DCM) = 0.43; Slow evaporation of DCM afforded clear, colorless needles. Collected 0.536 g, 19 % yield based on **2**. $^1\text{H-NMR}$ (CDCl_3): δ 4.68 br, s (NH_2), δ 7.687 s (C-H).
 - 2-amino-5,6-dichloropyrazine (5):** R_f (DCM) = 0.20; Slow evaporation of DCM afforded cream colored needles. Collected 0.756 g, 27 % yield based on **2**. $^1\text{H-NMR}$ (CDCl_3): δ 4.99 br, s (NH_2), δ 7.953 s (C-H).
- 3. Preparation of 1•CuBr.** A mixture of **1** (26.3 mg, 0.203 mmol) and CuBr_2 (23.0 mg, 0.103 mmol) in 5 mL of a 1:1:1 v/v/v mixture of Ace:EtOH:MeCN was gently refluxed for 15 min to give a clear, light yellow solution. The mixture was concentrated to ~1 mL by slow evaporation to afford a suspension of pale-yellow needles. The needles were collected by filtration, washed successively with a small volume of cold EtOH (3 mL), 10 mL of CHCl_3 and allowed to air dry; Collected 15.3 mg; Yield 54.4 % based on CuBr_2 . FT-ATR-IR (cm^{-1}) of **1•CuBr**: 3378 s, 3286 s, 3207 m, 3180 m, 3130 m, 3071 w, 3055 w, 1875 w, 1757 w, 1660 w, 1619 vs, 1517 s, 1453 s, 1437 s, 1320 s, 1238 m, 1198 s, 1110 vs, 1072 vs, 884 m, 819 s, 765 m, 741 w, 709 w, 682 w, 670 vw, 666 vw, 596 m, 563 w, 482 vs, 448 vs, 416 s. A comparison of the FT-ATR-IR (cm^{-1}) of ligand **1** and **1•CuBr** is illustrated in Figure S10.
- 4. Preparation of 2a•CuBr.** A mixture of **2** (15.1 mg, 0.117 mmol) and CuBr_2 (23.1 mg, 0.103 mmol) in 15 mL of a 1:1:1 v/v/v mixture of Ace:EtOH:MeCN was gently refluxed for 2 min to give a clear, light yellow solution. The mixture was concentrated to ~5 mL dryness by slow evaporation. The pale-yellow needles and a small amount of amber rhombic prisms were collected by filtration on a 10 mm medium sintered Pyrex Buchner funnel, washed with 10 mL of CHCl_3 and air dried; Collected 12.7 mg; Yield 39.8% based on CuBr_2 . FT-ATR-IR (cm^{-1}) of **2a•CuBr**: 3406 vs, 3311 br,vs, 3220 m, 3206 w, 3183 w, 3066 w, 1615 vs, 1510 s, 1460 vs, 1390 vs, 1306 vs, 1241 sh, w, 1209 s, 1201 sh, m, 1131 s, 1024 s, 913 w, 884 br, vs, 688 m, 658 w, 558 s, 433 s. A comparison of the FT-ATR-IR (cm^{-1}) of ligand **2**, **2a•CuBr**, **2b•CuBr**, and **2c•CuBr** is illustrated in Figure S11.

- 5. Preparation of 2b·CuBr.** A mixture of **2** (27.5 mg, 0.212 mmol) and CuBr₂ (22.9 mg, 0.103 mmol) in 5 mL of a 1:1:1 v/v/v mixture of Ace:EtOH:MeCN was gently refluxed for 15 min to give a clear, light yellow solution. Upon cooling to room temperature, a mixture of pale-yellow needles and amber rhombic prisms formed. The mixture was concentrated to dryness by slow evaporation. The crystalline mixture was washed three times with cold MeCN (2 mL) and the sparingly soluble amber rhombic prisms collected by filtration. The crystals were washed repeatedly with CHCl₃ (20 mL total) and air dried; Collected 18.9 mg; Yield 67.5 % based on CuBr₂. FT-ATR-IR (cm⁻¹) of **2b·CuBr**: 3407 vs, 3295 vs, 3220 m, 3186 m, 3139 w, 3067 vw, 3042 vw, 2941 vw, 1616 s, 1544 vw, 1521 s, 1449 s, 1388 s, 1324 m, 1318 sh, w, 1211 s, 1136 m, 1076 m, 1037 m, 923 vw, 908 vw, 895 m, 867 m, 682 vs, 600 w, 469 m, 435 m. A comparison of the FT-ATR-IR (cm⁻¹) of ligand **2**, **2a·CuBr**, **2b·CuBr**, and **2c·CuBr** is illustrated in Figure S11.
- 6. Preparation of 2c·CuBr.** A mixture of **2** (31.1 mg, 0.240 mmol) and CuBr₂ (22.9 mg, 0.103 mmol) in 12 mL of a 1:5 v/v mixture of Ace:EtOH was gently refluxed for 5 min to give a golden yellow solution. Upon cooling to room temperature, a mixture of small, slender golden-yellow needles and pale-yellow needles (*i.e.* **2b·CuBr**) were obtained. The solution was carefully decanted, and the crystals triturated with 2 mL of cold EtOH before collecting by filtration, washed with 5 mL of CHCl₃ and air dried. Collected 10.6 mg of the mixed crystalline product; Yield 45.0 % based on CuBr₂. FT-ATR-IR (cm⁻¹) of **2c·CuBr**: 3409 vs, 3306 br,vs, 3200 vw, 3176 w, 3066 w, 3018 w 1612 vs, 1578 sh, w, 1516 s, 1454 vs, 1388 vs, 1307 m, 1297 sh,m, 1208 s, 1201 sh, s, 1130 m, 1039 m, 1026 sh,m, 913 w, 895 br, m, 690 m, 659 w, 570 m, 524 s, 465 w, 436 m. A comparison of the FT-ATR-IR (cm⁻¹) of ligand **2**, **2a·CuBr**, **2b·CuBr**, and **2c·CuBr** is illustrated in Figure S11.
- Note.** Dissolving the crystals in MeCN and concentrating to dryness by slow evaporation afforded only pale-yellow needles (*i.e.* **2b·CuBr**) and amber rhombic prisms (*i.e.* **2a·CuBr**) as determined by optical microscopy and careful unit cell screening of several crystals.
- 7. Preparation of 3·CuBr. Method A.** A solution CuBr₂ (22.9 mg, 0.103 mmol) was gently refluxed in 15 mL of the 1:1:1 v/v/v mixture of Ace:EtOH:MeCN to give a yellow solution and while still hot, a warm solution of **3** (15.6 mg, 0.120 mmol) in 5 mL of a similar solvent mixture was slowly added. The mixture was concentrated by slow evaporation to ~2 mL to afford a bright yellow crystalline solid. The soluble fraction was carefully decanted and the crystalline solid washed with cold EtOH (3 mL), CHCl₃ (10 mL) and air dried. Collected 26.3 mg; Yield 92.9% based on CuBr₂. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of the soluble fraction. **Method B.** A mixture of **3** (27.7 mg, 0.214 mmol) and CuBr₂ (23.8 mg, 0.107 mmol) in 5 mL of a 1:1:1 v/v/v mixture of Ace:EtOH:MeCN was gently refluxed for 30 min to give a clear, light yellow solution. The mixture was evaporated to dryness, then boiled into MeCN (10 mL), hot filtered and concentrated to ~2 mL by slow evaporation to afford a bright-yellow crystalline solid that was collected by filtration, washed 5 mL of CHCl₃ and air dried. Collected 22.9 mg; Yield 78.7% based on CuBr₂. FT-ATR-IR (cm⁻¹) of **3·CuBr**: 3473 w, 3342 br, vs, 3267 s, 3204 m, 3154 vs, 3079 m, 2917 vw, 1642 sh, w, 1617 m, 1583 w, 1511 s, 1462 m, 1427 vw, 1413 w, 1350 m, 1244 s, 1196 s, 1133 w, 1058 s, 1101 s, 945 w, 880 w, 835 m, 728 m, 635 vw, 586 w, 516 w, 501 w, 488 sh, w, 419 vs. See Figure 12 for a comparison of the FT-ATR-IR (cm⁻¹) of ligand **3** and **3·CuBr**. **Note.** A comparison of the FT-ATR-IR (cm⁻¹) of **3·CuBr** obtained from the 1:1:1 reaction mixture and MeCN is illustrated in Figure S13.

8. Preparation of 4·CuBr. A mixture of **4** (33.4 mg, 0.204 mmol) and CuBr₂ (22.4 mg, 0.100 mmol) was gently refluxed in 5 mL of a 1:1:1 v/v/v mixture of ace:EtOH:MeCN to give a light-yellow solution. The mixture was evaporated to dryness by slow evaporation. The mixture was triturated with 5 mL of MeCN, filtered and the solution evaporated to dryness. The brown solid so obtained was washed with 2 mL of cold EtOH, collected by filtration, washed with 5 mL of CHCl₃ and air dried. Collected 17.3 mg. FT-ATR-IR (cm⁻¹) of the solid mixture containing **4·CuBr**: 3474 sh, w, 3453 w, 3369, br, s, 3302 vs, 3214 sh, s, 3182 vs, 3046 vs, 2921 vs, 2852 vs, 2689 br, vs 1741 m, 1628 vs, 1569 s, 1512 s, 1451 s, 1378 s, 1312 s, 1260 sh, w, 1220 br, vs, 1178 s, 1066 sh, s, 1032 br, vs, 944 s, 871 s, 799 s, 745 w, 720 w, 695 w, 671 s, 597 s, 517 s, 456 vs, 408 w. A comparison of the FT-ATR-IR (cm⁻¹) of ligand **4** and the solid mixture containing **4·CuBr** is illustrated in Figure S14.

Note. Clear, colorless needles suitable for single crystal X-ray diffraction were carefully picked from the solid mixture. Crystals of **CuBr·(MeCN)**⁵ were also identified by its unit cell and space group during crystal screening.

9. Preparation of 5·CuBr. A mixture of **5** (31.0 mg, 0.189 mmol) and CuBr₂ (21.0 mg, 0.0940 mmol) was gently refluxed in 5 mL of the 1:1:1 v/v/v mixture of ace:EtOH:MeCN for 15 min to give a light-yellow solution. The mixture was concentrated by slow evaporation to ~1 mL and the yellow needles were collected by filtration, washed with 5 mL of CHCl₃ and air dried. Collected 18.7 mg; Yield 64.7% based on CuBr₂. FT-ATR-IR (cm⁻¹) of **5·CuBr**: 3343 s, 3294 vs, 3200 m, 3168 m, 3086 w, 1625 s, 1561 m, 1512 m, 1458 m, 1412 m, 1304 m, 1230 s, 1204 m, 1104 br, vs, 980 s, 840 w, 807 m, 744 m, 715 w, 638 m, 614 w, 550 m, 502 w, 487 w, 467 vw. A comparison of the FT-ATR-IR (cm⁻¹) of ligand **5** and **5·CuBr** is illustrated in Figure S15.

10. Preparation of 6·CuBr. A mixture of **6** (32.5 mg, 0.198 mmol) and CuBr₂ (22.6 mg, 0.101 mmol) was gently refluxed in 5 mL of a 1:1:1 v/v/v mixture of ace:EtOH:MeCN for 15 min to give a bright-yellow solution. The mixture was concentrated to ~1 mL by slow evaporation to afford small yellow needles that were collected by filtration, washed with 5 mL of CHCl₃ and air dried. Collected 21.8 mg; Yield 70.1 % based on CuBr₂. FT-ATR-IR (cm⁻¹) of **6·CuBr**: 3418 vs, 3309 vs, 3203 w, 3167 w, 3059 w, 1795 w, 1611 vs, 1562 sh, w, 1509 w, 1448 vs, 1306 s, 1213 s, 1159 w, 1110 s, 897 s, 746 m, 677 m, 690 w, 522 w, 472 m, 410 vs. A comparison of the FT-ATR-IR (cm⁻¹) of ligand **6** and **6·CuBr** is illustrated in Figure S16.

11. Single Crystal X-ray Crystallography: Suitable single crystals of Cu(I)Br with the ligands **1-6** for structural determination were grown by slow evaporation of the reaction solvent mixture (typically 1:1:1 v/v/v Ace:EtOH:MeCN) or from neat MeCN. Single crystals of **2c·CuBr** were reliably obtained by slow cooling of a hot 5:1 (v/v) solvent reaction mixture of EtOH: Ace. In all cases, save for the sparingly soluble **2a·CuBr**, the crystals were all soluble in MeCN and recrystallization from this solvent was often possible without effecting phase purity.^a

The reflections of **1·CuBr**, **3·CuBr** and **5·CuBr** were collected on an Rigaku SuperNova diffractometer equipped with multilayer optics monochromated dual source (Cu and Mo) Atlas detector, using CuK α (1.54184 Å), while **2a·CuBr**, **2b·CuBr** and **2c·CuBr** were collected on a Rigaku SuperNova single-source Oxford diffractometer with an Atlas EoS CCD detector with multilayer optics to produce monochromated MoK α (0.71073 Å) radiation. The data collection, reductions for data sets collected on Rigaku instruments were performed using CrysAlisPRO⁶ and analytical face-index based absorption correction methods were applied. The reflections for **4·CuBr** and **6·CuBr** were collected on Bruker-Nonius Kappa CCD diffractometer with Apex-II CCD detector using graphite-monochromated MoK α (0.71073 Å) radiation. The data obtained was processed using the program COLLECT⁷ and HKL DENZO AND SCALEPACK.⁸ The intensities for data collected on the Bruker-Nonius Kappa diffractometer were corrected for absorption using SADABS⁹ with multi-scan absorption correction method. All structures were solved by intrinsic phasing (ShelXT)¹⁰ and refined on F^2 by full-matrix least-squares techniques with the ShelXL program in the Olex2 (v.1.2.10) software¹¹ package that utilizes the SHELXL-2013 module.¹² The structure of **3·CuBr** was refined as a two-component twin. All C-H and N-H hydrogen atoms were calculated to their optimal positions and treated as riding atoms using isotropic displacement parameters 1.2 (sp² group) larger than that of the host atom. The N-H hydrogen atoms were treated as sp² hybridized with AFIX 93 in all cases, unless otherwise noted. In special or difficult cases restraints (DELU, RIGU, DFIX) and constraints (EADP) were used during the modeling.

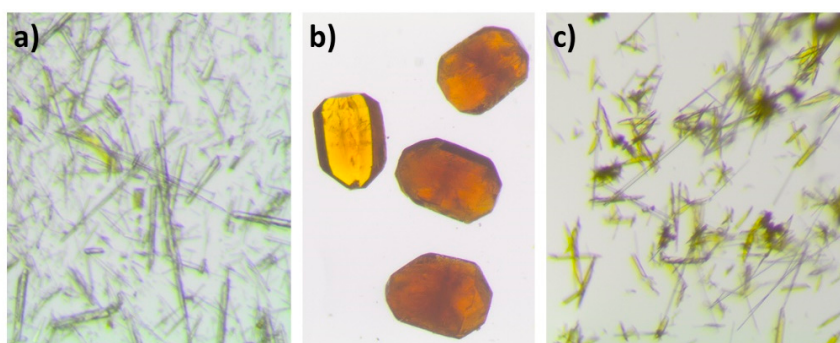


Figure S1. Crystal habit of a) clear, colorless needles **2a·CuBr**, b) prismatic blocks of **2b·CuBr** and c) a mixture of bright-yellow needles of **2c·CuBr** and some clear colorless needles of **2a·CuBr** viewed under diffuse light by optical microscopy.

^a The crystals of **2c·CuBr** were readily soluble in a small volume of MeCN to afford a greenish-yellow solution which only gave crystals of **2a·CuBr** and **2b·CuBr** upon evaporation as observed from the color and crystal habit by optical microscopy and unit cell screening of a minimum of ten crystals. In addition, the solid mixture of **4·CuBr** was soluble in MeCN, but the small size and poor crystallinity of the crystals was problematic throughout (See Figure S8 and S13).

Table S1. Single crystal X-ray experimental details for **2a·CuBr**, **2b·CuBr** and **2c·CuBr**.

Identification	2a·CuBr	2b·CuBr (2A5Cl_CuBr)	2c·CuBr
CCDC No.:	2001485	2001486	2001487
Empirical formula	C ₄ H ₄ BrClCuN ₃	C ₄ H ₄ BrClCuN ₃	C ₂ H ₂ BrCl _{0.5} CuN _{1.5}
Formula weight	273.00	273.00	208.23
Temperature/K	120.00(10)	120.00(10)	120.00(10)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pbcn</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	3.8240(2)	11.1836(3)	7.9322(7)
<i>b</i> /Å	11.2434(5)	12.3736(3)	4.0669(3)
<i>c</i> /Å	16.6051(6)	10.5430(3)	13.8656(14)
α /°	90	90	90
β /°	90	90	104.748(9)
γ /°	90	90	90
Volume/Å ³	713.93(6)	1458.96(7)	432.56(7)
<i>Z</i>	4	8	4
ρ_{calc} /g/cm ³	2.540	2.486	3.197
μ /mm ⁻¹	8.945	8.754	14.400
<i>F</i> (000)	520.0	1040.0	388.0
Crystal size/mm ³	0.231 × 0.024 × 0.014	0.088 × 0.06 × 0.023	0.128 × 0.022 × 0.013
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.376 to 59.146	4.91 to 58.094	6.076 to 57.642
Index ranges	-4 ≤ <i>h</i> ≤ 4, -14 ≤ <i>k</i> ≤ 8, -13 ≤ <i>l</i> ≤ 22	-15 ≤ <i>h</i> ≤ 15, -16 ≤ <i>k</i> ≤ 16, -13 ≤ <i>l</i> ≤ 12	-10 ≤ <i>h</i> ≤ 6, -4 ≤ <i>k</i> ≤ 5, -15 ≤ <i>l</i> ≤ 17
Reflections collected	2209	10496	1556
Independent reflections	1491 [<i>R</i> _{int} = 0.0304, <i>R</i> _{sigma} = 0.0615]	1781 [<i>R</i> _{int} = 0.0269, <i>R</i> _{sigma} = 0.0195]	932 [<i>R</i> _{int} = 0.0486, <i>R</i> _{sigma} = 0.1110]
Data/restraints/parameters	1491/0/91	1781/0/79	932/2/46
Goodness-of-fit on <i>F</i> ²	1.059	1.037	1.235
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0373, <i>wR</i> ₂ = 0.0776	<i>R</i> ₁ = 0.0243, <i>wR</i> ₂ = 0.0507	<i>R</i> ₁ = 0.0951, <i>wR</i> ₂ = 0.1866
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0445, <i>wR</i> ₂ = 0.0821	<i>R</i> ₁ = 0.0289, <i>wR</i> ₂ = 0.0523	<i>R</i> ₁ = 0.1249, <i>wR</i> ₂ = 0.2112
Largest diff. peak/hole / e Å ⁻³	0.69/-0.75	1.25/-0.87	1.52/-1.73
Flack parameter	-0.009(19)	NA	NA

Table S2. Single crystal X-ray experimental details for **1·CuBr**, **3·CuBr** and **4·CuBr**.

Identification	1·CuBr (2A3Cl_CuBr)	3·CuBr (2A6Cl_CuBr)	4·CuBr (2A56Cl_CuBr)
CCDC No.:	2001484	2001488	2001489
Empirical formula	C ₄ H ₄ BrClCuN ₃	C ₄ H ₄ BrClCuN ₃	C ₈ H ₆ BrCl ₄ CuN ₆
Formula weight	273.00	273.00	471.44
Temperature/K	120.01(10)	120.00(10)	170.00(10)
Crystal system	orthorhombic	monoclinic	triclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> /Å	20.0400(10)	3.8325(2)	3.8609(5)
<i>b</i> /Å	9.4312(6)	14.5560(9)	13.026(2)
<i>c</i> /Å	3.8277(3)	12.9398(6)	14.369(2)
α /°	90	90	94.709(11)
β /°	90	98.369(4)	95.994(11)
γ /°	90	90	90.960(5)
Volume/Å ³	723.44(8)	714.17(7)	716.07(19)
<i>Z</i>	4	4	2
ρ_{calc} /cm ³	2.507	2.539	2.186
μ /mm ⁻¹	13.486	13.661	5.057
<i>F</i> (000)	520.0	520.0	456.0
Crystal size/mm ³	0.278 × 0.025 × 0.014	0.078 × 0.053 × 0.01	0.12 × 0.04 × 0.01
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)	MoK α (λ = 0.71073)
2 θ range for data collection/°	8.826 to 148.948	6.072 to 147.228	4.064 to 55.762
Index ranges	-15 ≤ <i>h</i> ≤ 24, -10 ≤ <i>k</i> ≤ 11, -4 ≤ <i>l</i> ≤ 4	-4 ≤ <i>h</i> ≤ 4, -17 ≤ <i>k</i> ≤ 18, -10 ≤ <i>l</i> ≤ 15	-5 ≤ <i>h</i> ≤ 4, -15 ≤ <i>k</i> ≤ 17, -18 ≤ <i>l</i> ≤ 18
Reflections collected	2649	4314	5838
Independent reflections	1318 [<i>R</i> _{int} = 0.0515, <i>R</i> _{sigma} = 0.0624]	1432 [<i>R</i> _{int} = 0.0380, <i>R</i> _{sigma} = 0.0360]	3217 [<i>R</i> _{int} = 0.0810, <i>R</i> _{sigma} = 0.2104]
Data/restraints/parameters	1318/1/91	1432/0/74	3217/1/181
Goodness-of-fit on <i>F</i> ²	1.094	1.155	0.968
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0543, <i>wR</i> ₂ = 0.1520	<i>R</i> ₁ = 0.0650, <i>wR</i> ₂ = 0.1600	<i>R</i> ₁ = 0.0909, <i>wR</i> ₂ = 0.1890
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0612, <i>wR</i> ₂ = 0.1644	<i>R</i> ₁ = 0.0668, <i>wR</i> ₂ = 0.1612	<i>R</i> ₁ = 0.2004, <i>wR</i> ₂ = 0.2328
Largest diff. peak/hole / e Å ⁻³	1.13/-0.75	1.78/-1.00	1.45/-1.12
Flack parameter	-0.09(11)	NA	NA

Table S3. Single crystal X-ray experimental details for **5•CuBr** and **6•CuBr**.

Identification	5•CuBr (2A36Cl_CuBr)	6•CuBr (2A35Cl_CuBr)
CCDC No.:	2001490	2001491
Empirical formula	C ₄ H ₃ BrCl ₂ CuN ₃	C ₄ H ₃ BrCl ₂ CuN ₃
Formula weight	307.44	307.44
Temperature/K	120.00(10)	170.00(10)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	14.2159(10)	3.8252(2)
<i>b</i> /Å	3.9215(3)	19.2135(11)
<i>c</i> /Å	14.6851(9)	11.0159(6)
α /°	90	90
β /°	103.288(7)	99.377(3)
γ /°	90	90
Volume/Å ³	796.74(10)	798.80(8)
<i>Z</i>	4	4
ρ_{calc} /cm ³	2.563	2.556
μ /mm ⁻¹	15.378	8.334
<i>F</i> (000)	584.0	584.0
Crystal size/mm ³	0.613 × 0.033 × 0.03	0.16 × 0.06 × 0.06
Radiation	CuK α (λ = 1.54184)	MoK α (λ = 0.71073)
2 θ range for data collection/°	7.806 to 154.01	4.24 to 55.69
Index ranges	-17 ≤ <i>h</i> ≤ 16, -4 ≤ <i>k</i> ≤ 4, -18 ≤ <i>l</i> ≤ 18	-5 ≤ <i>h</i> ≤ 5, -24 ≤ <i>k</i> ≤ 25, -14 ≤ <i>l</i> ≤ 13
Reflections collected	6118	7241
Independent reflections	1661 [<i>R</i> _{int} = 0.0591, <i>R</i> _{sigma} = 0.0476]	1868 [<i>R</i> _{int} = 0.0584, <i>R</i> _{sigma} = 0.0695]
Data/restraints/parameters	1661/0/104	1868/0/100
Goodness-of-fit on <i>F</i> ²	1.058	1.047
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0451, <i>wR</i> ₂ = 0.1199	<i>R</i> ₁ = 0.0427, <i>wR</i> ₂ = 0.0654
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0563, <i>wR</i> ₂ = 0.1314	<i>R</i> ₁ = 0.0754, <i>wR</i> ₂ = 0.0730
Largest diff. peak/hole / e Å ⁻³	1.73/-0.85	0.64/-0.70

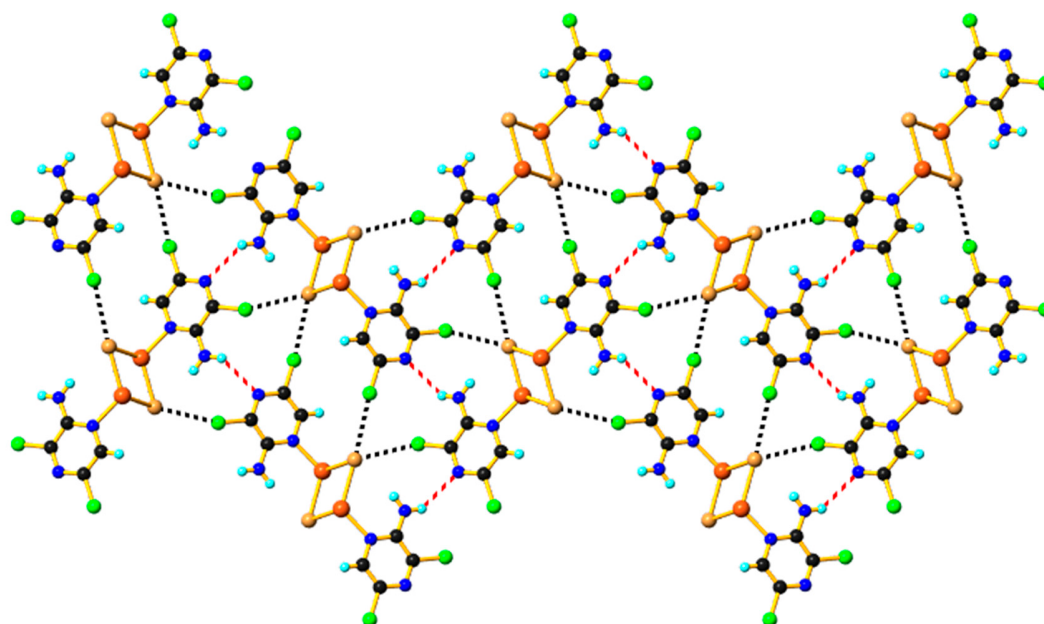


Figure S2. The herringbone packing arrangement of 1D polymeric chains of **6·CuBr**. Red- and black- dotted lines represent hydrogen and halogen bonds, respectively.

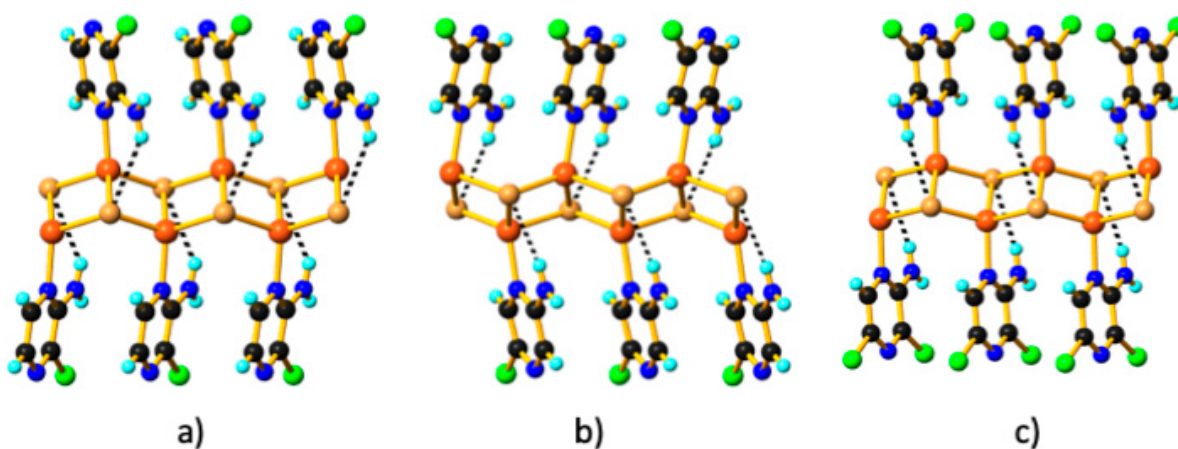


Figure S3. The 1D polymeric chains of a) **1·CuBr**, b) **2a·CuBr**, and c) **6·CuBr** displaying cyclic intrachain N–H···Br–Cu hydrogen bonds (black- dotted lines).

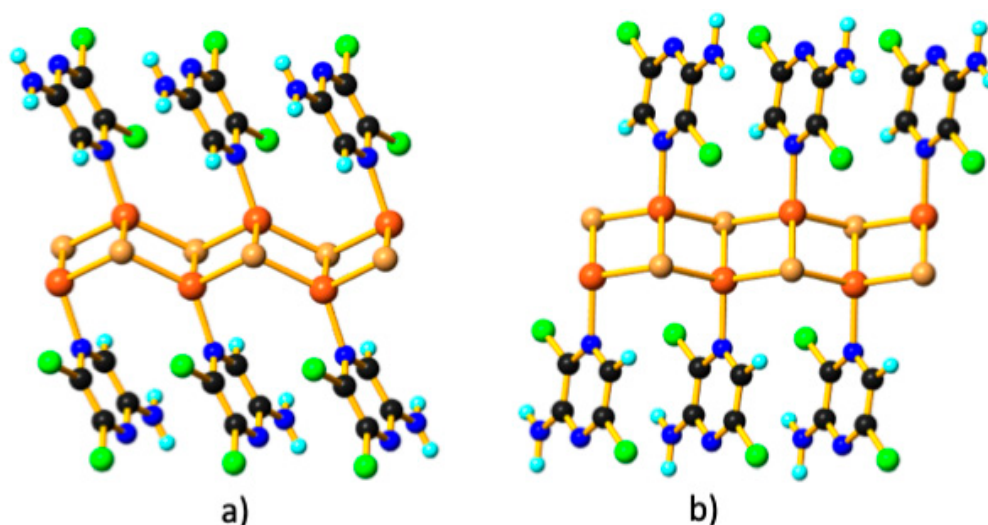


Figure S4. The 1D polymeric chains of a) $4 \cdot \text{CuBr}$, and b) $5 \cdot \text{CuBr}$.

12. Comments on Single Crystal X-ray Crystallography Data.

1·CuBr:

Alert level B

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds 0.0175 Ang.

Author comment: Crystals diffracted extremely weakly and multiple attempts were made to grow better quality crystals, but the long, slender needles required Cu radiation sources. Even with Cu radiation it was difficult to collect the high angle reflections and the combination of heavy and light atoms had a detrimental effect on the average bond precision values, but the structure was clearly established.

Alert level C

PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage

Author comment: Crystals diffracted extremely weakly and the molecular structure is non-chiral with a centrosymmetric space group, therefore the absolute configuration is irrelevant and the structure was clearly established.

2b·CuBr:

Alert level C

PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage 55 %

Author comment: The molecular structure is non-chiral with a centrosymmetric space group therefore the absolute configuration is irrelevant and the structure was clearly established.

2b·CuBr:

Alert level C

PLAT975_ALERT_2_C Check Calcd Resid. Dens. 0.73A From N2 0.57 eA-3

PLAT976_ALERT_2_C Check Calcd Resid. Dens. 1.08A From N2 -0.73 eA-3

PLAT977_ALERT_2_C Check Negative Difference Density on H2B -0.33 eA-3

Author comment: All three of these C-alerts arise from some unmodelled positional disordered of a Cl and NH2 group. Attempts to model this disorder were unsuccessful since occupancy of the heavier Cl is $\leq 5\%$.

2c·CuBr:

Alert level B

PLAT029_ALERT_3_B _diffn_measured_fraction_theta_full value Low . 0.952 Why?

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds 0.03 Ang.

Author comment: The crystals were small and diffracted weakly and attempts to obtain larger and better-quality crystals were unsuccessful. Icing during the data collection required the some of the most effected frames being exclude from the data reduction which are responsible for the low theta_full value. The weak diffraction, exclusion of frames had a detrimental effect on the bond precisions. Repeated data collections with Mo radiation sources provided consistent structural model.

3·CuBr:

Alert level B

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds 0.016 Ang.

Author comment: Crystals diffracted extremely weakly and multiple attempts were made to grow better quality crystals, but the small needles required Cu radiation sources. Even with Cu radiation it was difficult to collect the high angle reflections and the combination of heavy/light atoms and twinning had a detrimental effect on the average bond precision values, but the structure was clearly established.

4·CuBr:

Alert level B

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds 0.01925 Ang.

Author comment: The crystals were small and diffracted weakly and attempts to obtain larger and better-quality crystals were unsuccessful. Crystal twinning was frequently encountered which limited the number of suitable crystals. The weak diffraction had a detrimental effect on the bond precisions and on the overall quality of the data.

13. Powder X-ray Diffraction methods. The bulk samples of the chloro-substituted pyrazin-2-amines as Cu(I)Br complexes obtained as described in the experimental section, were analysed by powder X-ray diffraction (PXRD) using a PANalytical X'Pert PRO Alpha 1 diffractometer with Cu K α 1 radiation (1.54060 Å; 45 kV, 40 mA). Each sample was prepared on a silicon-made “zero-background signal generating” sample holder using petrolatum jelly as an adhesive. Diffraction intensities were acquired by an X'Celerator detector at room temperature with 2 θ -range of 4–60°, a step size of 0.017° and counting times of 40 s per step. The data processing and search-match phase analyses were made by program X'pert HighScore Plus v. 4.8.¹³ The unit cell parameters of the powder samples were determined by Pawley analysis¹⁴ using the corresponding single crystal structure parameters as the basis of least-squares refinements (variable parameters were as follows: zero-offset, polynomial background, sample displacement, unit cell and peak profile parameters). In some cases, no structural match could be found between the single crystal structure and the bulk material. Therefore, Pawley fits were done only to selected PXRD data in order to demonstrate their structural similarity to the corresponding single crystal structures. The biggest difference was observed for the complex crystal structure of **4•CuBr** which contains both Cu-coordinated and free, hydrogen-bonded ligand **4**. Based on the Pawley fit, the bulk phase of **4•CuBr** does not corresponded to that determined by single crystal X-ray analysis. While the single crystal structure obtained for **4•CuBr** contains additional un-complexed pyrazine ligand in the asymmetric unit, the best Pawley fit of **4•CuBr** suggests the bulk phase is isostructural to **6•CuBr**. Attempts to recrystallize this material have been unsuccessful to date, however, the PXRD (See Figure S and FT-IR (See Figure S) results are both consistent with one or more phases being present in the bulk material, as indicated by our current analysis. **CuBrCuBr**The best agreement was found for **1•CuBr**, **2b•CuBr**, **3•CuBr** and **6•CuBr** as displayed in the Pawley refinements.

Table S4. Refined unit cell				
	PXRD	SC-XRD	PXRD	SC-XRD

parameters of 1-CuBr and 2b-CuBr determined by the powder X-ray diffraction Pawley analysis of bulk powder (PXRD, at 293 K) shown with corresponding single crystal data (SCXRD). Parameters				
	1-CuBr (2A3Cl_CuBr)		2b-CuBr (2A5Cl_CuBr)	
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	<i>Pna2₁</i>	<i>Pna2₁</i>	<i>Pbcn</i>	<i>Pbcn</i>
<i>a</i> /Å	20.107(1)	20.0400(10)	11.2212(6)	11.1836(3)
<i>b</i> /Å	9.4837(6)	9.4312(6)	12.4084(7)	12.3736(3)
<i>c</i> /Å	3.8784(2)	3.8277(3)	10.6413(6)	10.5430(3)
α /°	90	90	90	90
β /°	90	90	90	90
γ /°	90	90	90	90
<i>V</i> /Å ³	739.55(8)	723.44(8)	1481.66(14)	1458.96(7)
<i>R</i> _{exp.}	0.076		0.069	
<i>R</i> _{prof.}	0.091		0.084	
<i>R</i> _{w-prof}	0.114		0.101	
<i>R</i> ₁		0.0543		0.0243
<i>wR</i> ₂		0.1520		0.0507
<i>GOF</i>	1.499	1.094	1.473	1.037

Table S5. Refined unit cell parameters of **3-CuBr (2A6Cl_CuBr)** determined by the powder X-ray diffraction Pawley analysis of bulk powder (PXRD, at 293 K) shown with corresponding single crystal data (SCXRD).

Parameters	PXRD	SC-XRD
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> /Å	3.8848(2)	3.8325(2)
<i>b</i> /Å	14.6610(8)	14.5560(9)
<i>c</i> /Å	13.0073(7)	12.9398(6)
α /°	90	90
β /°	95.014(8)	98.369(4)
γ /°	90	90

$V/\text{\AA}^3$	730.67(7)	714.17(7)
$R_{\text{exp.}}$	0.0719	
$R_{\text{prof.}}$	0.141	
$R_{\text{w-prof}}$	0.192	
R_1		0.0650
wR_2		0.1600
GOF	2.668	1.155

Table S6. Refined unit cell parameters of **4·CuBr** and **6·CuBr** determined by the powder X-ray diffraction Pawley analysis of bulk powder (PXRD, at 293 K) shown with corresponding single crystal data (SCXRD).

Parameters	PXRD	SC-XRD	PXRD	SC-XRD
4·CuBr (256Cl_CuBr)		6·CuBr (2A35Cl_CuBr)		
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P-1$	$P2_1/c$	$P2_1/c$
$a/\text{\AA}$	3.7884(5)	3.8609(5)	3.8079(3)	3.8252(2)
$b/\text{\AA}$	19.223(2)	13.026(2)	19.199(1)	19.2135(11)
$c/\text{\AA}$	11.104(1)	14.369(2)	11.0962(7)	11.0159(6)
$\alpha/^\circ$	90	94.709(11)	90	90
$\beta/^\circ$	99.339(1)	95.994(11)	99.3003(8)	99.377(3)
$\gamma/^\circ$	90	90.960(5)	90	90
$V/\text{\AA}^3$	797.93(16)	716.07(19)	800.57(9)	798.80(8)
$R_{\text{exp.}}$	0.068		0.082	
$R_{\text{prof.}}$	0.123		0.095	
$R_{\text{w-prof}}$	0.169		0.132	
R_1		0.0810		0.0584
wR_2		0.2104		0.0695
GOF	2.479	0.968	1.624	1.047

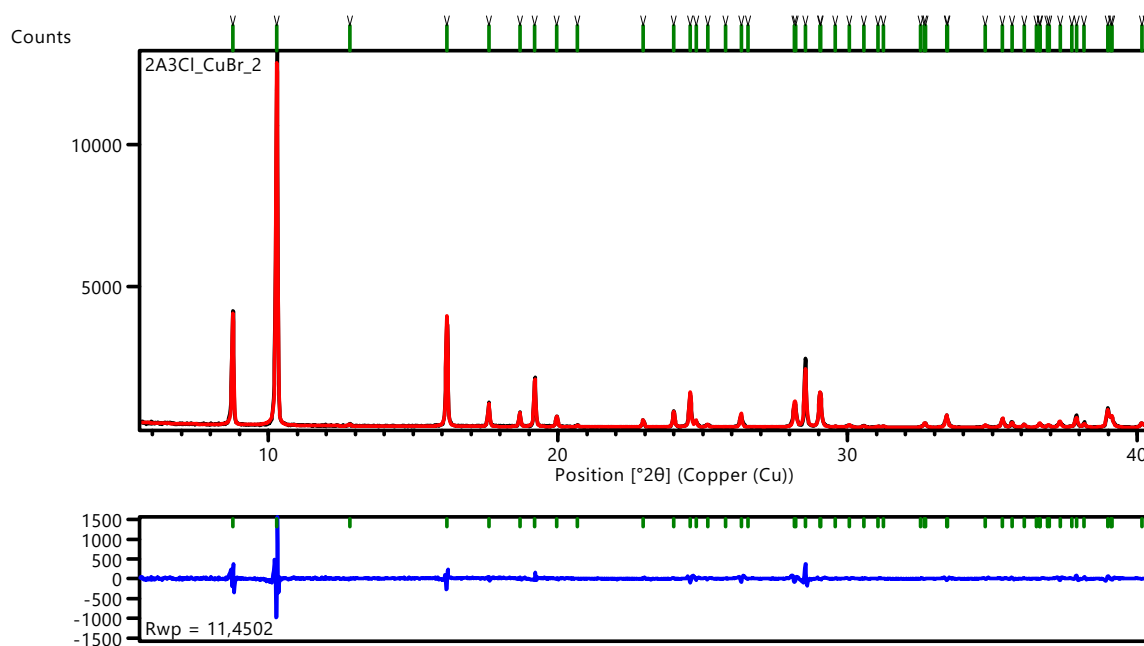


Figure S5. Pawley refinement plot of **1·CuBr (2A3Cl_CuBr)**. Experimental pattern is shown in black and refined profile in red, whereas green colored ticks correspond to Bragg peak positions of the refined unit cell. Difference plot of experimental vs. refined profile is shown below in blue.

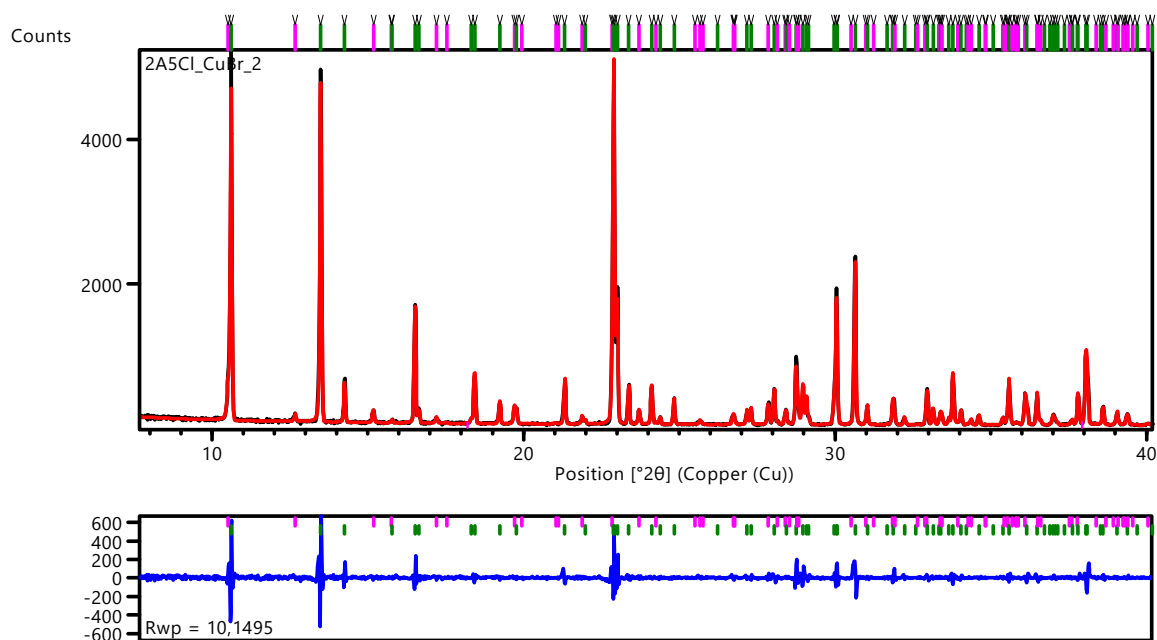


Figure S6. Pawley refinement plot **2b·CuBr (2A5Cl_CuBr)**. Experimental pattern is shown in black and refined profile in red, whereas green and pink colored ticks correspond to Bragg peak positions of

2b·CuBr and minor impurity phase that was identified as **2·CuBr₂**,¹⁵ respectively. Difference plot of experimental vs. refined profile is shown below.

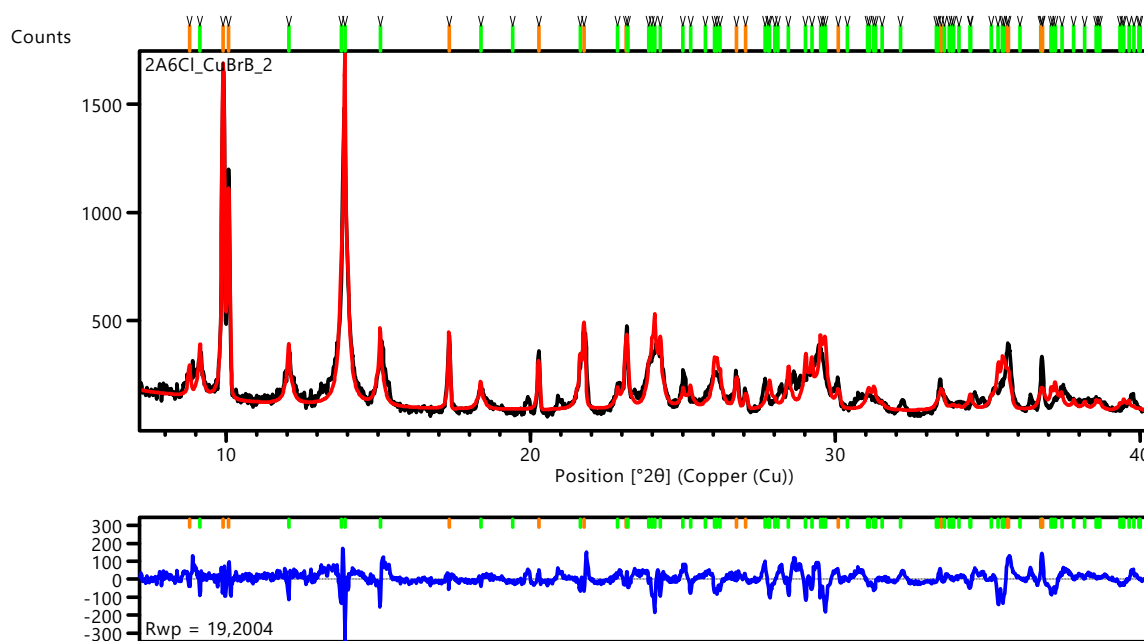


Figure S7. Pawley refinement plot of **3·CuBr (2A6Cl_CuBr)**. Experimental pattern is shown in black and refined profile in red, whereas green and orange colored ticks correspond to Bragg peak positions of

3·CuBr and minor impurity phase that remained unidentified, respectively. Difference plot of experimental vs. refined profile is shown below.

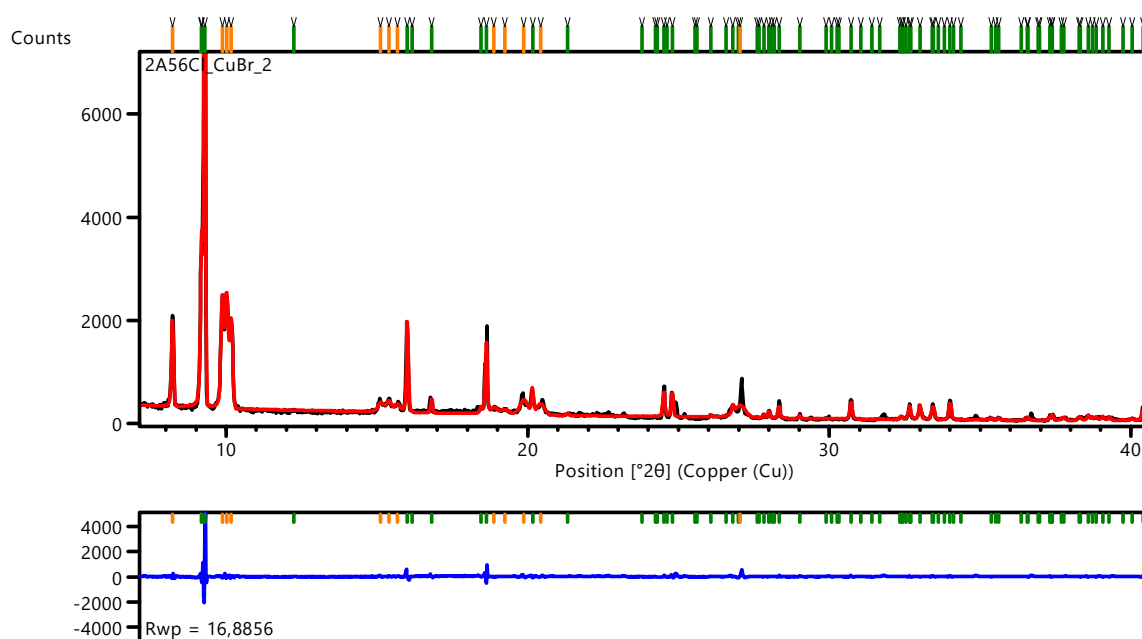


Figure S8. Pawley refinement plot of **4·CuBr** (2A56Cl_CuBr). Experimental pattern is shown in black and refined profile in red, whereas green, and orange colored ticks correspond to Bragg peak positions of isostructural unit cell of **6·CuBr**, and to a phase that remained unidentified, respectively. Difference plot of experimental vs. refined profile is shown below.

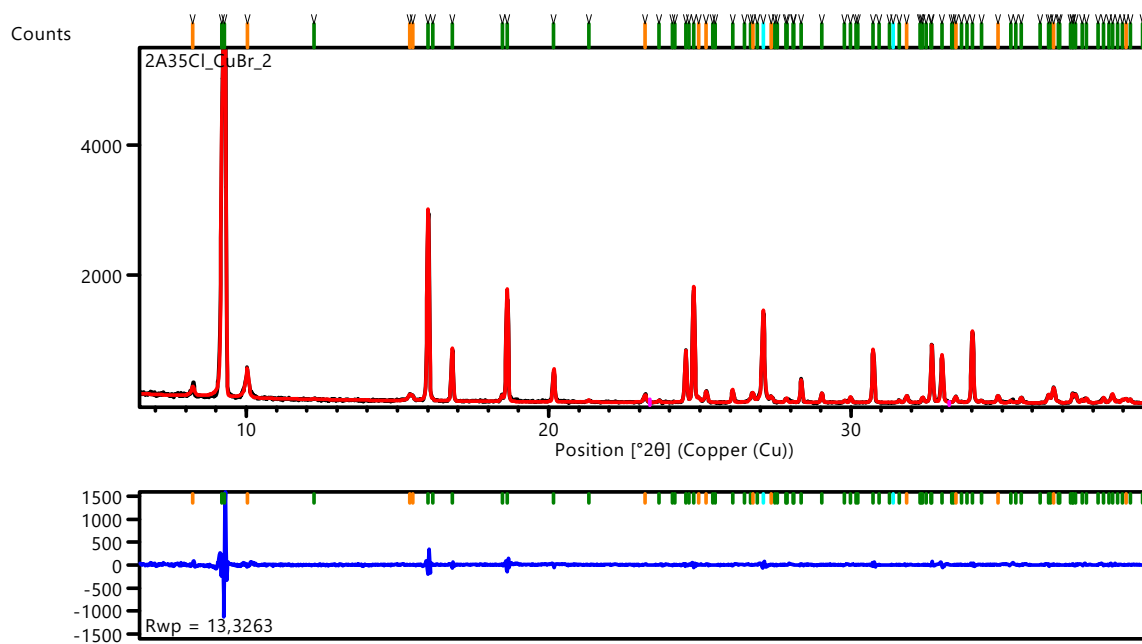


Figure S9. Pawley refinement plot **6·CuBr (2A35Cl_CuBr)**. Experimental pattern is shown in black and refined profile in red, whereas green, cyan, and orange colored ticks correspond to Bragg peak positions of **6·CuBr**, minor residual phases of CuBr, and a phase that remained unidentified, respectively. Difference plot of experimental vs. refined profile is shown below.

14. FT-ATR-IR methods and figures. All FT-IR spectra were recorded on a Bruker Alpha Platinum single reflection diamond ATR module using 24 scans at 4 cm^{-1} resolution over a range of $4000\text{--}400\text{ cm}^{-1}$ for both the collected data and background correction. Solid crystalline samples were gently ground before placing on the ATR stage and the spectra were baseline corrected and smoothed using adjacent averaging over 15 sample points. Normalized % transmittance spectra of the free ligand (X) and the X·Cu(I)Br complex are illustrated as stack plots below. Abbreviations used in the experimental section (br = broad, sh = shoulder, vs = very strong, s = strong, m = medium, w = weak, vw = very weak).

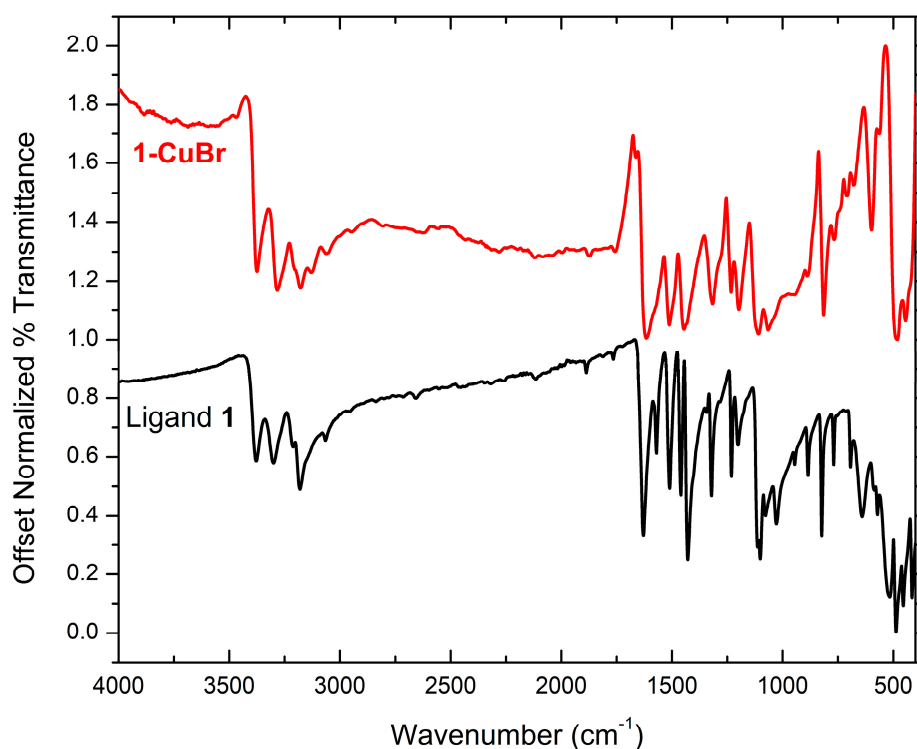


Figure S10. FT-ATR-IR (cm^{-1}) of **1** and **1·CuBr**

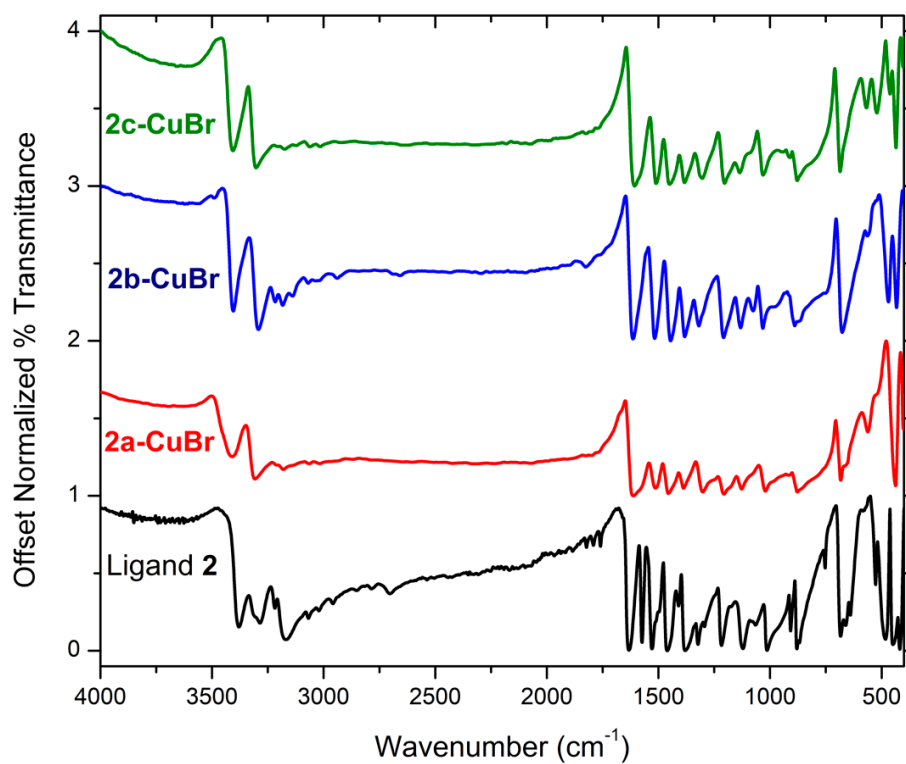


Figure S11. FT-ATR-IR (cm⁻¹) of **2**, **2a·CuBr**, **2b·CuBr**, and **2c·CuBr**

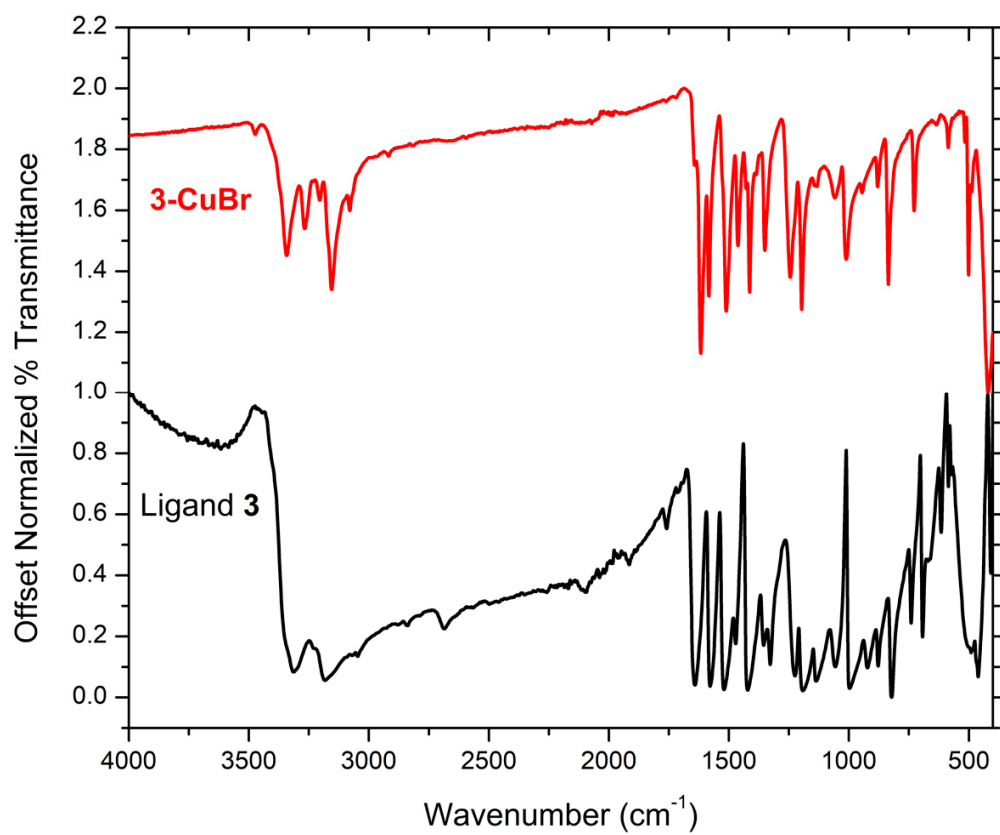


Figure S12. FT-ATR-IR (cm^{-1}) of **3** and **3-CuBr**

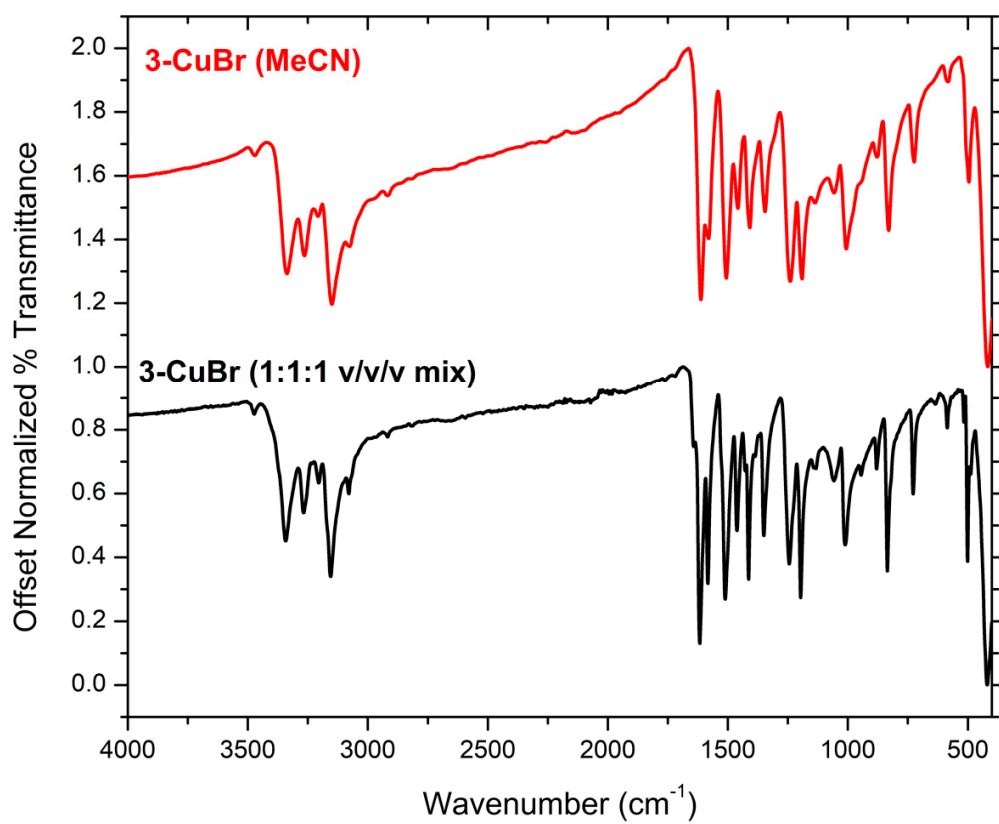


Figure S13. FT-ATR-IR (cm^{-1}) of **3-CuBr** obtained from the 1:1:1 v/v/v Ace:EtOH:MeCN mixture and the **3-CuBr** obtained from MeCN.

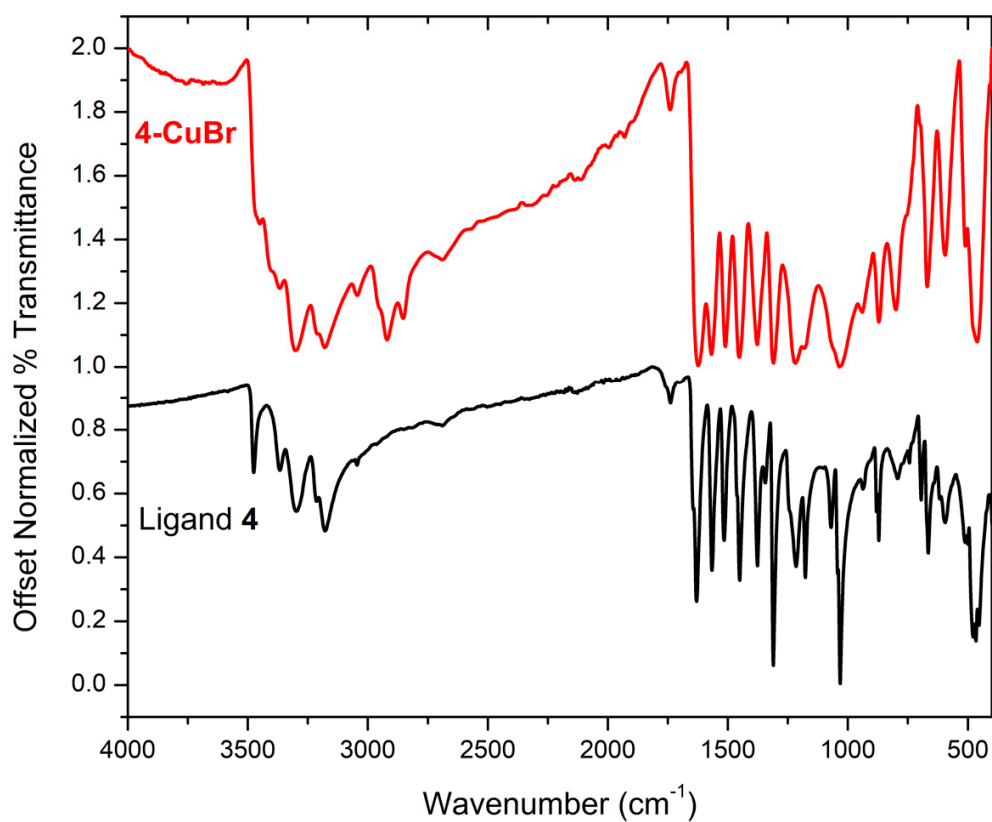


Figure S14. FT-ATR-IR (cm⁻¹) of **4** and the solid mixture containing **4·CuBr**.^b

^b Based on PXRD analysis this material did not contain any crystalline material consistent with the structure obtained by single crystal X-ray crystallography, therefore the IR spectra labelled as **4·CuBr** is not representative of this complex obtained by single crystal X-ray analysis and is only given for comparison to the ligand **4**.

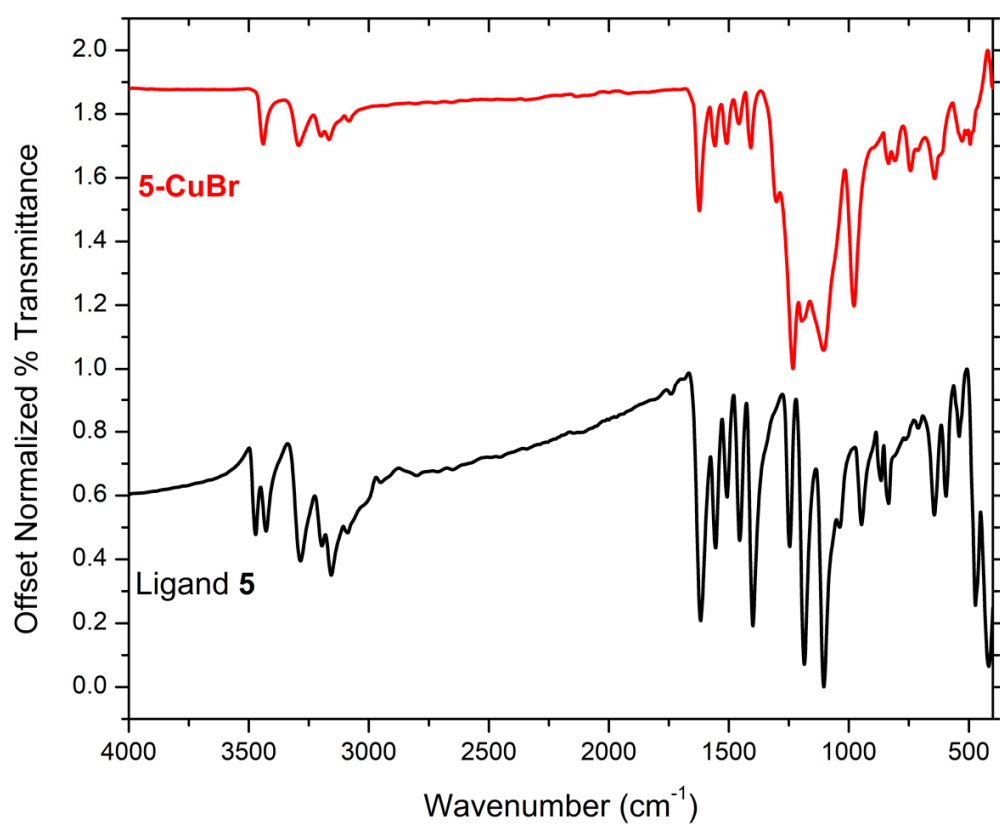


Figure S15. FT-ATR-IR (cm⁻¹) of **5** and **5·CuBr**

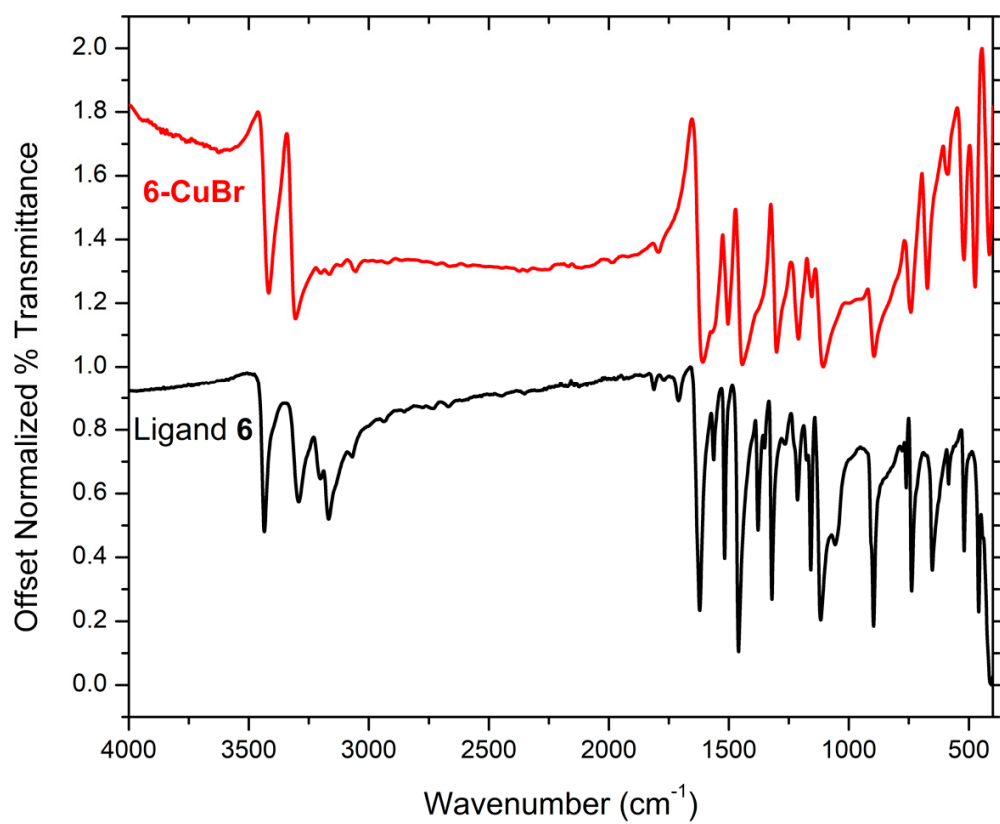


Figure S16. FT-ATR-IR (cm^{-1}) of **6** and **6-CuBr**

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