Building a Two-dimensional Co-ordination Polymer having a Multilayered Arrangement. A Molecular Assembly comprising Hanging Phenazine Molecules between Polymeric Stair Frameworks of Copper(I) Halides†

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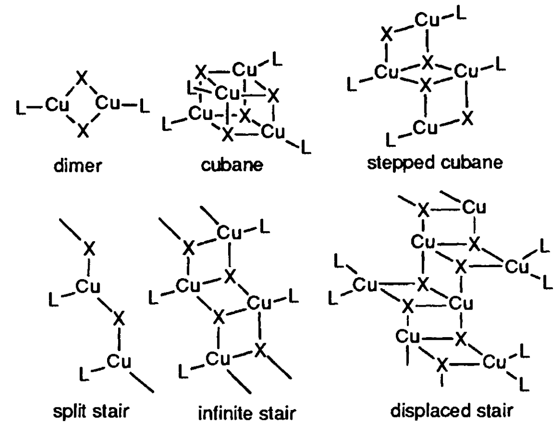
Three copper(I) complexes with phenazine (phz), $[\{Cu_2(\mu\text{-}X)_2(\mu\text{-phz})\}_\infty]$ (X = I **1**, Br **2** or Cl **3**) were synthesized and their molecular structures and packing determined by single-crystal X-ray diffraction methods. The copper atoms of the Cu_2I_2 rhomboid in **1** are bridged by phz molecules to give an infinite linear chain and the phz molecules overlap between the infinite chains with an interplanar spacing of 3.46 Å. Compounds **2** and **3** have two-dimensional sheets of hanging phz molecules between polymeric stair frameworks of CuBr and CuCl, respectively. The interplanar spacings of adjacent phz molecules for **2** and **3** are 3.40 and 3.36 Å, respectively. All three complexes exhibit an absorption band at about 710 nm characteristic of copper(I) co-ordination polymers with phz.

A large number of copper(I) complexes exhibit intense optical absorption due to metal-to-ligand charge-transfer (m.l.c.t.) bands. In the photoexcited state the metal can participate in redox reactions, some of which have potential practical applications.[1] Extensive studies have been reported on the mechanism of the intramolecular electron transfer induced by irradiating monomeric copper species in solution. On the other hand little work has been performed on photoactive copper(I) polymers with stacks of aromatic ligands because of synthetic difficulties. Copper(I) co-ordination polymers, $[\{Cu(CN)(dmphen)\}_\infty]$, $[\{Cu(SCN)(dmphen)\}_\infty]$ and $[\{Cu_3(CN)_3(bquin)_2\}_\infty]$, having a stacked layer arrangement have been prepared and spectroscopically characterized,[2,3] where dmphen and bquin are 2,9-dimethyl-1,10-phenanthroline and 2,2′-biquinoline, respectively.

In an attempt to prepare copper(I) complex assemblies with stacks of aromatic systems we previously treated $[Cu(C_2H_4)]Y$ (Y = ClO_4, PF_6 or NO_3) or AgY (Y = ClO_4 or NO_3) with phenazine (phz) and obtained several multilayered assemblies and co-ordination polymers. Copper(I) and silver(I) complexes with phenazine were synthesized:[4] $[Cu_2(phz)_3(MeOH)_2][PF_6]_2\cdot phz$ has infinite stacks of alternating unco-ordinated phz molecules and complex cations $[Cu_2(phz)_3(MeOH)_2]^{2+}$ and gives a characteristic c.t. band at 710 nm; the polynuclear complex $[\{Ag_2(phz)(NO_3)_2\}_\infty]$ has stacks of phz molecules between two-dimensional sheets consisting of six-membered rings of Ag^I bonded to phz and NO_3^-.

Copper(I) halide complexes with unidentate ligands have been widely studied structurally, and are notable for the variety of stoichiometries and structural formats displayed. Stoichiometries Cu:X:ligand of 1:1:0.5, 1:1:1, 1:1:1.5, 1:1:2 and 1:1:3 have been observed.[5] Normally the 1:1:3 complexes[6,7] are monomers, 1:1:2 complexes are monomers[7] or rhombs[7-9] and 1:1:0.5 complexes are chairs.[10] On the other hand, 1:1:1 complexes give a variety of structures, dimer,[11] tetramers[7,8,12-15] of cubane and stepped cubane types, polymers[11] of stair, split and displaced stair types (Scheme 1).



Scheme 1

Our interest in copper(I) halide complexes focuses on building molecular assemblies with nitrogen-containing bases.

We report here the synthesis, structures and properties of new copper(I) halide complex polymers having multilayered arrangements of phenazine.

Experimental

General.—All operations were carried out under argon and ethylene by using standard Schlenk or vacuum-line techniques. Solid-state ^{13}C–^{1}H cross-polarization (CP) NMR experiments, with magic angle spinning (MAS), were performed on a JEOL GSX-270 spectrometer equipped with a NM-G27MU accessory. Rotation speeds of 3.3–4.0 kHz were employed. All reported peak positions are relative to tetramethylsilane. Electronic spectra were recorded on a Hitachi spectrometer. Acetonitrile was purified according to the literature,[16] as was reagent-grade copper(I) chloride.[17] Copper(I) bromide and iodide were used without further purification. Reagent-grade phenazine was obtained from Wako Pure Chemical. All other chemicals of reagent grade were used without further purification.

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† *Supplementary data available:* See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Crystal data for [{$Cu_2(\mu$-$X)_2(\mu$-phz)}$_\infty$] (X = I **1**, Br **2** or Cl **3**)

	1	**2**	**3**
Formula	$C_3H_2Cu_{0.5}I_{0.5}N_{0.5}$	C_6H_4BrCuN	C_6H_4ClCuN
M	140.28	233.55	189.10
Colour	Reddish brown	Black	Black
Crystal size/mm	0.20 × 0.20 × 0.10	0.10 × 0.10 × 0.04	0.15 × 0.05 × 0.1
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/m$	$P\bar{1}$	$P\bar{1}$
a/Å	14.830(4)	8.786(1)	8.812(3)
b/Å	9.323(2)	9.334(1)	9.216(2)
c/Å	5.0012(6)	3.9772(4)	3.810(2)
α/°	90.00	91.31(1)	91.93(3)
β/°	96.48(2)	101.10(1)	100.69(4)
γ/°	90.00	68.60(1)	111.53(2)
U/Å^3	687.1(2)	296.41(7)	281.1(2)
Z	8	2	2
D_c/g cm^{-3}	2.712	2.617	2.234
2θ/°	2–55	2–55	2–55
No. of unique data used ($\lvert F\rvert > 3\sigma\lvert F_o\rvert$)	847	1360	1282
R	0.028	0.039	0.027
R'	0.040	0.054	0.038
F(000)	516	222	186
μ/cm^{-1}	75.37	102.55	42.52

Syntheses.—[{$Cu_2(\mu$-$I)_2(\mu$-phz)}$_\infty$] **1**. Copper(I) iodide (19.1 mg, 10 mmol dm^{-3}) and phenazine (9.0 mg, 5.0 mmol dm^{-3}) were stirred in acetonitrile (10 cm^3) for 1 h at 70 °C under an argon atmosphere. The pale yellow mixture was sealed in a glass tube under an argon atmosphere. After standing for 3 d in a Dewar bottle filled with water at 70 °C deep reddish brown plate crystals were obtained (yield 45%) (Found: C, 26.20; H, 1.45; N, 5.20. C_6H_4CuIN requires C, 25.70; H, 1.45; N, 5.00%).

[{$Cu_2(\mu$-$Br)_2(\mu$-phz)}$_\infty$] **2**. Copper(I) bromide (14.3 mg, 10 mmol dm^{-3}) and phenazine (9.0 mg, 5.0 mmol dm^{-3}) were stirred in acetonitrile (10 cm^3) for 1 h at 70 °C under an argon atmosphere. The pale yellow mixture was sealed in a glass tube under an argon atmosphere. After standing for 5 d in a Dewar bottle filled with water at 70 °C black needle crystals were obtained (yield 46%) (Found: C, 30.90; H, 1.75; N, 6.15. C_6H_4BrCuN requires C, 30.85; H, 1.70; N, 6.00%).

[{$Cu_2(\mu$-$Cl)_2(\mu$-phz)}$_\infty$] **3**. Copper(I) chloride (9.9 mg, 10 mmol dm^{-3}) and phenazine (9.0 mg, 5.0 mmol dm^{-3}) were stirred in acetonitrile (10 cm^3) for 1 h at 70 °C under an argon atmosphere. The pale yellow mixture was sealed in a glass tube under an argon atmosphere. After standing for 7 d in a Dewar bottle filled with water at 70 °C black needle crystals were obtained (yield 46%) (Found: C, 38.65; H, 2.30; N, 7.70. C_6H_4ClCuN requires C, 38.10; H, 2.15; N, 7.40%).

Table 2 Atomic coordinates for non-hydrogen atoms of complexes **1**–**3** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Complex **1**			
I(1)	0.132 17(2)	0	0.328 94(8)
Cu(1)	0	0.135 40(7)	$\frac{1}{2}$
N(1)	0	0.348 8(4)	$\frac{1}{2}$
C(1)	0.054 1(2)	0.423 4(3)	0.684 4(6)
C(2)	0.112 8(3)	0.350 0(4)	0.885 7(7)
C(3)	0.167 0(3)	0.423 3(4)	1.071 6(7)
Complex **2**			
Br(1)	0.298 88(7)	0.103 02(6)	0.212 6(1)
Cu(1)	0.450 4(1)	0.156 50(8)	−0.211 0(2)
N(1)	0.482 2(6)	0.358 2(5)	−0.097(1)
C(1)	0.366 5(7)	0.494 9(6)	−0.238(1)
C(2)	0.222 0(7)	0.499 6(6)	−0.489(2)
C(3)	0.106 3(9)	0.634 6(8)	−0.635(2)
C(4)	0.126 0(8)	0.775 7(6)	−0.542(2)
C(5)	0.258 6(8)	0.777 9(6)	−0.305(2)
C(6)	0.383 9(7)	0.639 1(6)	−0.144(1)
Complex **3**			
Cu(1)	0.548 57(5)	0.153 59(4)	0.330 2(1)
Cl(1)	0.688 12(9)	0.101 17(8)	−0.112 7(2)
N(1)	0.516 9(3)	0.355 3(3)	0.419 1(6)
C(1)	0.904 8(4)	0.637 1(4)	0.253 1(9)
C(2)	0.783 1(4)	0.498 2(3)	0.280 9(8)
C(3)	0.635 7(3)	0.494 9(3)	0.391 0(7)
C(4)	0.381 0(3)	0.359 7(3)	0.530 2(7)
C(5)	0.252 6(4)	0.217 0(3)	0.571 2(8)
C(6)	0.886 5(4)	0.780 5(4)	0.324 9(9)

X-Ray Data Collection, Structure Solution and Refinement.—Diffraction data were obtained on a Rigaku AFC-5R four-circle diffractometer at ambient temperature with Mo-Kα radiation (λ 0.710 69 Å). Crystal data and details of measurements for the copper(I) complexes with phenazine **1**–**3** are summarized in Table 1. Standard reflections were monitored every 50 measurements and the decay in their intensities was within 5%. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.

The structures were solved by a direct method[18] and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations. Reliability factors are defined as $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$ and $R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$, where $w = 4F_o^2/\Sigma\sigma^2(F_o)^2$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[19] Hydrogen atoms were included as a fixed contribution in the last cycle; their thermal parameters were assumed to be isotropic. The calculations were performed on a VAX computer using the TEXAN program system.[20] The final R and R' values were 0.028 and 0.040 for complex **1**, 0.039 and 0.054 for **2**, 0.027 and 0.038 for **3**, respectively. The final positional coordinates for non-hydrogen atoms of complexes **1**–**3** are given in Table 2, selected bond distances and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Structure of Complex **1**.—Considering the higher co-ordination ability of halide ions, we first synthesized the copper co-ordination polymer with phz and iodide, **1**. The copper atom

Table 3 Selected distances (Å) and angles (°) for complexes **1**–**3** with e.s.d.s in parentheses

	1 (X = I)	**2** (X = Br)	**3** (X = Cl)
Cu(1)–N(1)	1.989(4)	2.030(4)	2.005(2)
Cu(1)–X(1)	2.5585(6)	2.515(1)	2.397(1)
Cu(1)–X(1′)	2.5585(6)	2.614(1)	2.487(1)
Cu(1)–X(1″)		2.536(1)	2.406(2)
Cu(1)···Cu(1′)	2.525(1)	3.141(2)	3.049(1)
Cu(1)···Cu(1″)		3.641(2)	3.467(2)
Cu(1)···Cu(1‴)		3.977(0)	3.810(2)
N(1)–Cu(1)–X(1)	119.56(1)	107.74(12)	124.96(7)
N(1)–Cu(1)–X(1′)	119.56(1)	122.7(1)	122.97(7)
N(1)–Cu(1)–X(1″)		124.97(13)	108.19(8)
X(1)–Cu(1)–X(1′)	120.87(3)	104.49(3)	89.54(4)
X(1)–Cu(1)–X(1″)		103.90(3)	105.00(4)
X(1′)–Cu(1)–X(1″)		90.03(3)	102.90(5)

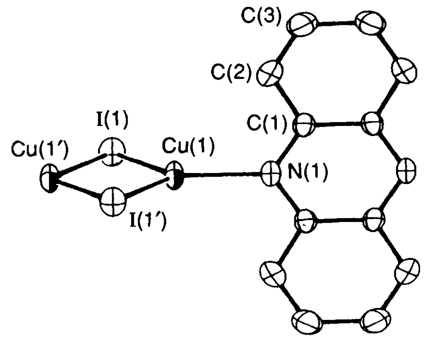


Fig. 1 Molecular structure of $[\{Cu_2(\mu\text{-}I)_2(\mu\text{-}phz)\}_\infty]$ **1**

in **1** is co-ordinated to two bridging iodides and one nitrogen atom of a bridging phz molecule in a trigonal geometry as shown in Fig. 1, the bond angles N(1)–Cu(1)–I(1) and I(1)–Cu(1)–I(1′) being 119.56(1) and 120.87(3)°, respectively. The bond angle N(1)–Cu(1)–Cu(1′) is 180(1)° and **1** forms an infinite linear chain. This is the first three-co-ordinate copper(I) complex with a four-membered $Cu(\mu\text{-}I)_2Cu$ ring bridged by ligand, although the $[Cu_2(\mu\text{-}I)_2(ligand)_2]$ dimers and four-co-ordinate copper polymers with polymeric stairs are well known. The Cu–N distance of 1.989(4) Å and Cu–I distance of 2.5585(6) Å are within those of 1.95–2.20 and 2.55–2.66 Å respectively reported for three-co-ordinate copper(I) with NI_2 donor sets.[11,15,21] The Cu···Cu distance of 2.525(1) Å is shorter than that 2.56 Å of metallic copper and 2.54–2.66 Å in $[\{Cu(\mu\text{-}I)(nitrile)\}_\infty]$ with polymeric stairs.[15] The phz molecules of the linear chain are in the same plane. The dihedral angle between the phz molecule and the Cu_2I_2 plane is 75.28° in the linear chain. The packing arrangement is shown in Fig. 2(*a*) which indicates the overlap of the phz molecules between the infinite linear chains. The interplanar spacing of 3.46 Å between two phz molecules indicates the existence of π–π interaction [Fig. 2(*b*)] and is comparable to 3.36 Å in $[\{Ag(phz)ClO_4\}_\infty]$ having infinite linear chains –phz–Ag–phz–Ag–, where only part of the phz molecules is overlapped because of the presence of the counter anion ClO_4^- between the linear chains.[22] On the other hand the co-ordination of the counter anion iodide to copper made it possible to increase the degree of superposition of the phz molecules in the packing arrangement of **1**: the phz molecules overlap with *ca.* 50% sliding of the molecules relative to each other [Fig. 2(*b*)].

Structure of Complex **2**.—The copper(I) complex with phz, **2**, was synthesized using bromide in the place of iodide in order to change the structural framework. Fig. 3 depicts a segment of the two-dimensional structure. The Cu(1) is co-ordinated in a distorted-tetrahedral geometry to one nitrogen atom of phz and three bromide ions, the six bond angles around Cu being 90–125°. The Cu–N distance of 2.030(4) Å and average Cu–Br distance of 2.56 Å are slightly longer than 1.94–1.96 and average 2.52 Å for $[\{Cu(\mu\text{-}Br)(nitrile)\}_\infty]$ with polymeric stairs, and the Cu···Cu distance of 3.391(2) Å (average) is longer than the 3.02–3.07 Å for the nitrile complexes.[15] Fig. 4 shows views of the two-dimensional sheet of phz molecules between the polymeric stairs, consisting of Cu and Br atoms, and indicates the overlap between adjacent phz molecules with an interplanar distance of 3.40 Å. This is the first example of a two-dimensional sheet of ligands hanging between a copper halide framework which resembles a bookshelf.

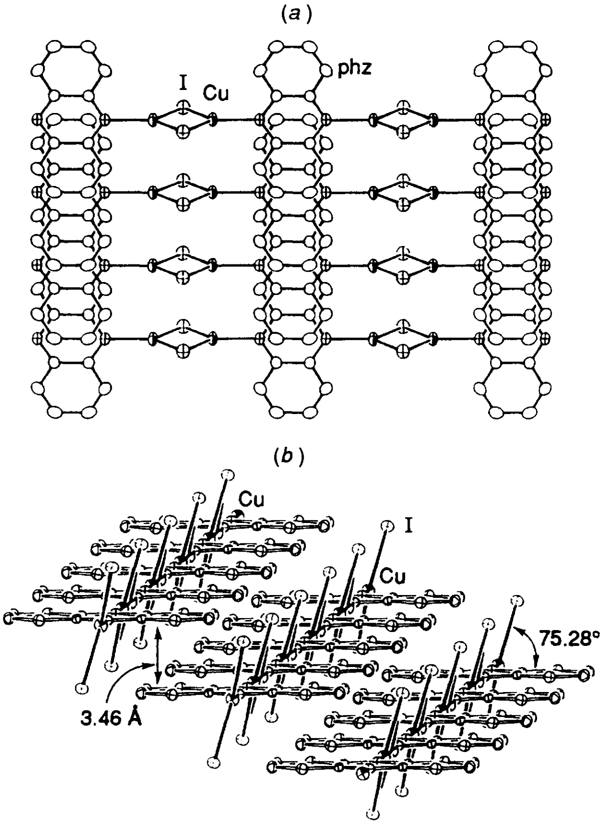


Fig. 2 Top (*a*) and side views (*b*) of the packing arrangement of complex **1**

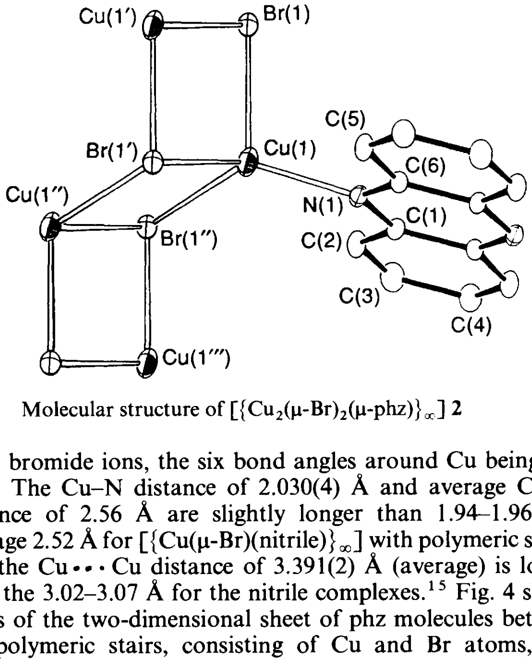


Fig. 3 Molecular structure of $[\{Cu_2(\mu\text{-}Br)_2(\mu\text{-}phz)\}_\infty]$ **2**

In the case of other counter anions such as ClO_4^- and PF_6^-, copper(I) is not co-ordinated to the anions and forms infinite stacks of alternating unco-ordinated phz molecules and complex cations $[Cu_2(phz)_3(MeOH)_2]^{2+}$, and a segregated column of the mononuclear complex $[Cu(phz)_2(H_2O)]^+$, respectively.[22] Bis[2-(phenylamino)-1,10-phenanthroline]dicopper(I) crystallizes to form herringbone stacking.[23] The

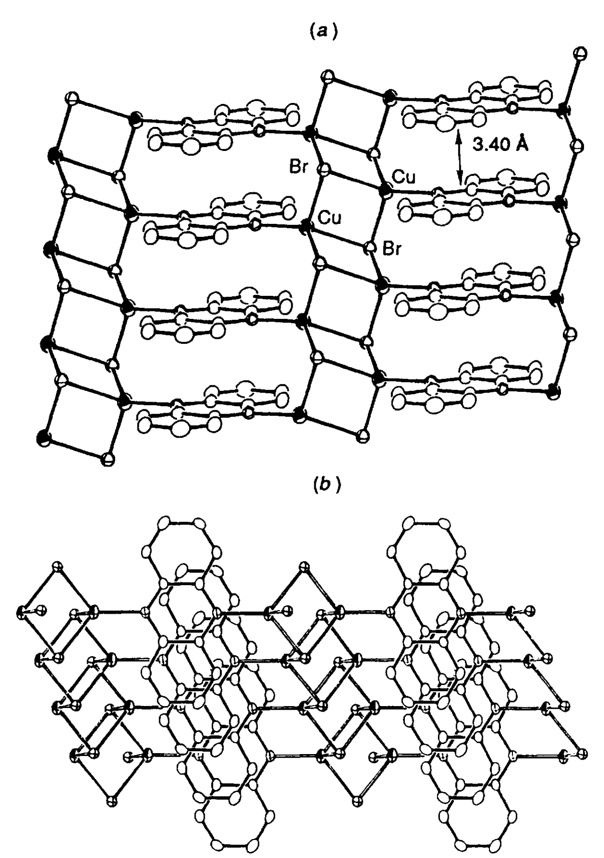


Fig. 4 Top (*a*) and side views (*b*) of the packing arrangement of complex **2**

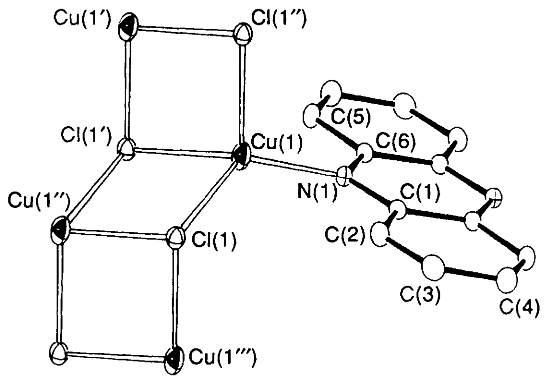


Fig. 5 Molecular structure of $[\{Cu_2(\mu\text{-}Cl)_2(\mu\text{-phz})\}_\infty]$ **3**

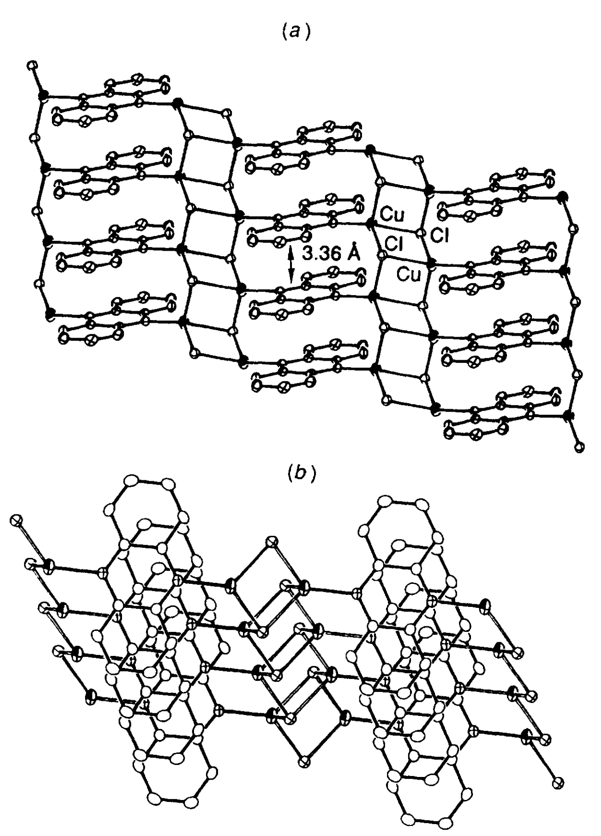
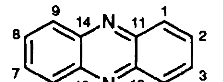


Fig. 6 Top (*a*) and side views (*b*) of the packing arrangement of complex **3**



crystal structures of $[\{Cu(dmphen)(CN)\}_\infty]$, $[\{Cu(dmphen)(NCS)\}_\infty]$ and $[\{Cu_3(bquin)_2(CN)_3\}_\infty]$ consist of zigzag chains of copper(I) linked by CN^- and NCS^- to form stacks of dmphen molecules as described above.[2,3] These interesting compounds are, however, one-dimensional molecular assemblies. Other copper(I) halide and pseudo-halide complexes with N-containing ligands so far reported are also of the common one-dimensional 'stair' polymer type.[15] Thus, complex **1** is notable as a two-dimensional multilayered assembly with stacks of aromatic compounds.

Structure of Complex **3**.—It was interesting to see whether a polymeric stair framework is formed in the presence of chloride, because the copper halide framework is changed from rhomboidal to polymeric stair on going from bromide to iodide as described above. The molecular structure of complex **3** was found to be a two-dimensional sheet with a polymeric stair framework similar to that of **2** as shown in Fig. 5. The copper is co-ordinated in a distorted-tetrahedral geometry to one nitrogen atom of phz and three chloride ions. The Cu–N distance of 2.005(2) Å is shorter than the 2.030(4) Å in **2**, and the Cu $\cdots$ Cu distances 3.258(1) Å (average) are shorter than the 3.391(2) Å (average) in **2**. Thus, there is no drastic change in the crystal structure between **2** and **3**.

Copper(I) chloride complexes with pyridine $[\{Cu(\mu\text{-}Cl)(py)\}_\infty]$ (py = pyridine) adopt a one-dimensional structure with a polymeric stair framework consisting of Cu and Cl, and can be considered to be an example of a complex with 'monodentate' phz. Both the Cu–N and Cu–Cl distances of $[\{Cu(\mu\text{-}Cl)(py)\}_\infty]$, 1.993(8) and 2.419(4) Å (average), are shorter than the corresponding values in **3**. This indicates that the polymeric stair framework is more highly strained in **3** with bridging phz than that in $[\{Cu(\mu\text{-}Cl)(py)\}_\infty]$ with monodentate py. Fig. 6 shows the top and side views of the two-dimensional multilayered sheet with polymeric stair framework consisting of Cu and Cl atoms. The interplanar spacing of 3.36 Å is shorter than the 3.40 Å in **2**, indicating that it is regulated by the halide ions. This fact is of particular importance.

Solid-state ^{13}C NMR Spectra.—Solid-state CP MAS ^{13}C NMR spectra of the co-ordination polymers were measured, since the polymers are insoluble in usual solvents. Complex **2** exhibited two resonances at δ 129.7 and 138.5 assigned to $C^{1-4,6-9}$ and C^{11-14} of phz, respectively, the corresponding chemical shift of free phz being δ 129.0 and 141.4, respectively. Similarly two resonances for **3** were observed at δ 128.9 and 137.5. On the other hand three resonances were observed for **1** at δ 127.9, 131.8 and 139 assigned to $C^{2,3,7,8}$, $C^{1,4,6,9}$ and C^{11-14} of phz, respectively. The resonances of the quaternary atoms C^{11-14} adjacent to the nitrogen atoms are shifted upfield

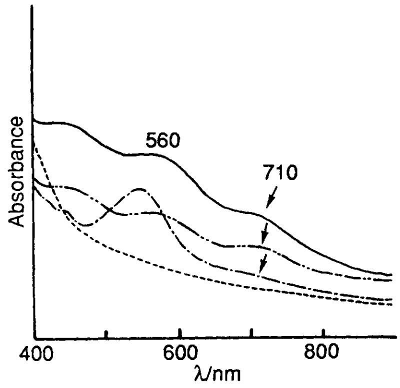


Fig. 7 Electronic spectra of complexes **1** (— · —), **2** (— · · —) and **3** (——) (KBr disc) compared with that of free phz (– – –)

upon co-ordination of phz to copper. The co-ordination shifts are larger than those for other carbons and increase in the order **1**(−2.4) < **2**(−2.9) < **3**(−3.9 ppm) which is consistent with the decreasing interplanar spacing: **1**(3.46) > **2**(3.40) > **3**(3.36 Å).

Electronic Spectra.—Fig. 7 shows the solid-state (KBr disc) electronic spectra of complexes **1**–**3**. Complexes **2** and **3** exhibit bands at about 450 and 560 nm which are assigned to copper(I)-to-ligand charge-transfer bands. Another band was observed at 710 nm. Three bands were also found for **1** at about 440, 543 and 710 nm. The band at 710 nm is considered to be characteristic of copper(I) co-ordination polymers with phz rather than charge transfer from unco-ordinated to co-ordinated phz.[22]

In conclusion we have synthesized and characterized molecular assemblies comprising hanging phz molecules between copper halide frameworks. The rhomboidal frameworks of Cu_2I_2 form linear chains with phz to give stacks of phz molecules with interplanar spacings of 3.46 Å between the chains. On the other hand the polymeric stair frameworks of CuBr and CuCl give two-dimensional multilayered arrangements of phenazine, the interplanar spacings of adjacent phz molecules being 3.40 and 3.36 Å, respectively. Thus the copper halide frameworks are very useful for building copper molecular assemblies, regulating the molecular structure and packing. It is noted that these molecular assemblies have an absorption band at about 710 nm characteristic of copper(I) co-ordination polymers with phz.

Acknowledgements

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