Syntheses, Structures and Properties of Copper(I) Co-ordination Polymers with Bridging Phenazine: Construction of One- and Two-dimensional Structures with π–π Stacking of Phenazine†

Takayoshi Kuroda-Sowa,*[a] Megumu Munakata,*[a] Hajime Matsuda,[a] Shin-ichi Akiyama[a] and Masahiko Maekawa[b]

[a] *Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan*
[b] *Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577, Japan*

Four novel copper(I) phenazine (phz) compounds, $[\{Cu(phz)(NO_3)\}_\infty]$ **1**, $[\{Cu(acr)_2(NO_3)\}_2(phz)(H_2O)]$ **2** (acr = acridine), $[\{Cu_2(phz)(PFO_3)\}_\infty]$ **3** and $[\{[Cu(phz)(MeCN)]_2(C_{16}H_{10})(PF_6)_2\}_\infty]$ **4** ($C_{16}H_{10}$ = pyrene) have been synthesized and their molecular structures and packing have been determined by single-crystal X-ray diffraction methods. The copper atoms in **1** are bridged by phz forming an infinite one-dimensional zigzag chain. These bridging phz molecules have a π–π interaction between neighbouring chains forming an infinite columnar stack of phz molecules. The monomer complex, **2**, has an infinite columnar stack of metal-free phz and metal-co-ordinated acr. Copper(I) atoms in **3** are bridged by phz and $PFO_3{}^{2-}$ alternately. The resulting one-dimensional chains are connected through a tetradentate, asymmetric $PFO_3{}^{2-}$ bridge, with π–π interaction between the phz molecules forming an infinite two-dimensional sheet structure. The backbone of compound **4** is almost the same as in **1** except that a pyrene molecule is intercalated into every other phz stack in a one-dimensional chain. The electrical conductivity of compound **3** and $[\{[Cu(phz)(MeCN)]_2(C_{16}H_{10})(PF_6)_2I_{1.3}\}_\infty]$ **5**, obtained by iodine doping of compound **4** were $1 \times 10^{-7.6}$ and $1 \times 10^{-4.7}$ S cm^{-1}, respectively. The electronic absorption bands of compounds **1**, **3** and **4** which appeared around 700 nm are characteristic of copper(I) co-ordination polymers with bridging phz.

A variety of choice in linking ligands together with the different transition-metal co-ordination geometries exhibited makes co-ordination polymer chemistry a fruitful research field. One remarkable example is CuL_2 (L = 2,5-dimethyl-*N*,*N*′-dicyano-1,4-benzoquinone diimine)[1,2] whose structure is characterized by the *coexistence* of a π–π stacking structure of the quinone diimines and a three-dimensional scaffolding structure composed of tetrahedral copper centres bridged by quinone diimines through co-ordination bonds. The metallic conductivity of this compound down to 1.3 K is related to the mixed-valence copper atoms (average $+\frac{4}{3}$)[3] which results from the coexistence of different types of packing forces.

Phenazine (phz) is well known as an electron donor which can form a columnar stack through π–π interaction. Alternating stacks of phz and electron acceptors such as 1,2,4,5-benzenetetracarboxylic dianhydride[4] or 7,7,8,8-tetracyano-*p*-quinodimethane[5] are observed in crystal structures. Moreover phz can act as a linking ligand in transition-metal complexes by co-ordination through its two nitrogen atoms, although few complexes have been structurally characterized.[6,7] Recently we reported several interesting crystal structures of complexes of copper(I) or silver(I) with phz.[8,9] Copper(I) halides with phz, $[\{Cu_2(\mu\text{-}X)_2(phz)\}_\infty]$[8] have one-dimensional chain (X = I) or two-dimensional sheet (X = Cl or Br) structures composed of $(CuX)_2$ moieties connected by phz, together with interchain or intrasheet phz π–π interactions, respectively. As for the silver(I) complexes,[9] $[\{Ag(phz)(ClO_4)\}_\infty]$ has a one-dimensional chain structure with interchain phz π–π interactions, while $[\{Ag_2(phz)(NO_3)_2\}_\infty]$ has a two-dimensional sheet structure with intersheet π–π interaction. However, non-halide copper(I) complexes with phz so far reported are not polymeric but monomeric or dimeric such as $[Cu(phz)_2(NO_3)]$ or $[\{Cu_2(phz)_3(MeOH)_2\}(phz)(PF_6)_2]$.[9] In this paper we describe the syntheses and structures of four novel non-halide copper(I) phz complexes, three of which have one- or two-dimensional polymeric structures together with π–π stacking of phz. Electrical conductivity and electronic transitions of these polymer compounds are also discussed.

Experimental

All operations were carried out under argon or ethylene by using standard Schlenk or vacuum-line techniques. Tetrakis(acetonitrile)copper(I) hexafluorophosphate was synthesized and purified using the literature method.[10] Acetone treated with potassium permanganate was dried over potassium carbonate and distilled immediately before use. Benzene was distilled from sodium–benzophenone under argon immediately before use and methanol was dehydrated on magnesium cake and distilled immediately before use. All other chemicals of reagent grade were purchased from Wako Pure Chemical and were used without further purification. Electronic spectra (400–900 nm) were recorded on a Hitachi 150–20 spectrophotometer using KBr discs.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared and these should be handled with great care.

Syntheses.—$[\{Cu(phz)(NO_3)\}_\infty]$ **1**. Several pieces of copper metal (3 × 3 × 1 mm) were added to a solution of copper(II) nitrate trihydrate (9.6 mg, 4.0×10^{-2} mmol) in acetone (6 cm^3)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

and stirred for 30 min under ethylene. To the resultant copper(I) solution phz (14.4 mg, 8.0 × 10^{-2} mmol) in acetone (4 cm^3) was added and stirred for 10 min under argon. The orange solution was sealed in a glass tube and after 10 d at room temperature orange plate crystals were obtained. λ_{max}(KBr disc)/nm 560 (sh) and 700.

[{Cu(acr)$_2$(NO$_3$)}$_2$(phz)(H$_2$O)] **2**. Several pieces of copper metal (3 × 3 × 1 mm) were added to a solution of copper(II) nitrate trihydrate (9.6 mg, 4.0 × 10^{-2} mmol) in methanol (6 cm^3) and stirred for 30 min under ethylene. The atmosphere was changed to argon and the solution was added to phz (28.8 mg, 0.16 mmol) and stirred for 20 min, then a solution of acridine (acr) (28.7 mg, 0.16 mmol) in methanol (4 cm^3) was added to the above solution and stirred for 20 min more. The resultant solution was filtered and the orange filtrate was sealed in a glass tube. After standing for 5 d at 0 °C, red columnar crystals were obtained (Found: C, 65.95; H, 3.90; N, 10,45. $C_{64}H_{42}Cu_2N_8O_7$ requires C, 65.90; H, 3.95; N, 9.60%). λ_{max}(KBr disc)/nm 500 (sh).

[{Cu$_2$(phz)(PFO$_3$)}$_\infty$] **3**. A solution of phz (13.0 mg, 7.2 × 10^{-2} mmol) in acetone–benzene (4:5 v/v, 9 cm^3) was added to tetrakis(acetonitrile)copper(I) hexafluorophosphate (13.4 mg, 3.6 × 10^{-2} mmol) and stirred for 50 min under argon. The resultant orange solution was sealed in a glass tube. After standing for 6 months at ambient temperature, black plate crystals were obtained. λ_{max}(KBr disc)/nm 560 (sh) and 710.

[{[Cu(phz)(MeCN)]$_2$(C$_{16}$H$_{10}$)(PF$_6$)$_2$}$_\infty$] **4**. A solution of phz (32.5 mg, 0.18 mmol) in acetone (4 cm^3) was added to a solution of tetrakis(acetonitrile)copper(I) hexafluorophosphate (13.4 mg, 3.6 × 10^{-2} mmol) in acetone (3 cm^3) and stirred for 15 min under argon. A solution of pyrene ($C_{16}H_{10}$) (18.2 mg, 9.0 × 10^{-2} mmol) in acetone (3 cm^3) was added to the above solution and stirred for 15 min. The resultant orange solution was sealed in a glass tube. After standing for 7 d at − 15 °C, red columnar crystals were obtained (Found: C, 49.80; H, 2.95; N, 8.30. $C_{22}H_{16}CuF_6N_3Cu$ requires C, 49.75; H, 3.05; N, 7.90%). λ_{max}(KBr disc) nm 560 (sh) and 700.

[{[Cu(phz)(MeCN)]$_2$(C$_{16}$H$_{10}$)(PF$_6$)$_2$I$_{1.3}$}$_\infty$] **5**. Crystals of compound **4** were ground and sealed in one arm of a glass tube which contained an excess of iodine in the other arm. After standing for 7 d at 50 °C, black powders were obtained. The iodine content was determined on the basis of the elemental analysis (Found: C, 42.95; H, 2.60; N, 6.60. $C_{44}H_{32}Cu_2F_{12}I_{1.3}N_6P_2$ requires C, 43.10; H, 2.65; N, 6.85%).

X-Ray Data Collection, Structure Solution and Refinement.—Diffraction data for all compounds were collected at ambient temperature using the ω–2θ scan technique on a Rigaku AFC5R or AFC6S four-circle diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout the data collection for each compound indicating crystal and electronic stability. Azimuthal scans of several reflections for each compound did not indicate a need for an absorption correction except for compound **3**, for which an empirical absorption correction was applied which resulted in transmission factors ranging from 0.81 to 1.00. The data were corrected for Lorentz and polarization effects. Crystal data and details of measurements for the copper(I) complexes **1**–**4** are summarized in Table 1.

The structures were solved by direct methods.[11] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations. Hydrogen atoms were included but not refined. Reliability factors are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 4F_o^2/\Sigma\sigma^2(F_o)^2$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[12] The calculations were performed on a VAX computer using the program system TEXSAN-TEXRAY.[13] The final R and R' values were 0.030 and 0.036 for **1**, 0.056 and 0.065 for **2**, 0.033 and 0.045 for **3**, and 0.043 and 0.047 for **4**, respectively. The slightly greater R values for **2** are caused by a water molecule incorporated into the crystal lattice. The final parameters for the non-hydrogen atoms of compounds **1**–**4** are given in Tables 2–5, respectively, and selected bond distances and angles are listed in Table 6. Dihedral angles and interplane distances of planes defined by phz, acr or pyrene molecules are listed in Table 7.

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

Table 1 Crystal data for [{Cu(phz)(NO$_3$)}$_\infty$] **1**, [{Cu(acr)$_2$(NO$_3$)}$_2$(phz)(H$_2$O)] **2**, [{Cu$_2$(phz)(PFO$_3$)}$_\infty$] **3** and [{[Cu(phz)(MeCN)]$_2$-(C$_{16}$H$_{10}$)(PF$_6$)$_2$}$_\infty$] **4**

	1	**2**	**3**	**4**
Formula	$(C_{12}H_8CuN_3O_3)_\infty$	$C_{64}H_{40}Cu_2N_8O_7$	$(C_{12}H_{12}Cu_2FN_2O_3P)_\infty$	$(C_{44}H_{32}Cu_2F_{12}N_6P_2)_\infty$
M	305.76	1160.16	405.27	1061.80
Colour, habit	Orange, plate	Red, prism	Black, plate	Red, prism
Crystal size/mm	0.10 × 0.25 × 0.25	0.25 × 0.30 × 0.30	0.20 × 0.10 × 0.20	0.20 × 0.15 × 0.15
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	*Pcca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	13.132(2)	10.614(4)	7.622(3)	10.101(2)
b/Å	5.290(3)	13.452(8)	17.413(3)	12.793(3)
c/Å	16.479(1)	10.126(4)	4.990(1)	8.301(1)
α/°	90.000	97.45(4)	93.61(2)	95.94(2)
β/°	90.000	107.10(3)	108.96(2)	93.37(2)
γ/°	90.000	99.40(4)	95.15(2)	79.35(2)
U/Å^3	1144.8(10)	1338(1)	620.9(3)	1047.7(7)
Z	4	1	2	1
D_c/g cm^{-3}	1.774	1.439	2.167	1.683
Diffractometer (RIGAKU)	AFC5R	AFC6S	AFC5R	AFC5R
μ/cm^{-1}	19.17	8.57	35.84	11.85
$2\theta_{max}$/°	55.1	55.0	55.0	55.0
h,k,l	0–16, 0–6, −20 to 0	0–13, −17 to 15, −12 to 12	0–9, −22 to 22, −6 to 6	0–12, −16 to 16, −10 to 10
No. of unique data used ($\|F\| > 3\sigma\|F_o\|$)	1472	2987	2215	2606
F(000)	616.00	594.00	400.00	534.00
R,[a] R'[b]	0.030, 0.036	0.056, 0.065	0.033, 0.045	0.043, 0.047

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Electrical Conductivity Measurements.—Electrical conductivity was measured by a conventional two-probe method at ambient temperature. The sample was placed in a bakelite cylinder (inner diameter 3 mm) and both ends of the cylinder were capped by copper electrodes. Pressure was applied between the electrodes using a vice and the highest conductivity was recorded on a digital multimeter.

Results

Structure of Compound **1**.—In a previous paper[9] we showed that copper(I) and phzenazine in methanol solution give a mononuclear complex [Cu(phz)$_2$(NO$_3$)] which has a four-co-ordinate copper(I) centre bonded to the two nitrogen atoms of the two phenazine molecules and to the two oxygen atoms of the NO$_3^-$ anion. When the solvent was changed from methanol to acetone, compound **1** with its one-dimensional polymeric structure was obtained. It seems reasonable that the high solubility of the monomer complex in acetone compared to that in methanol causes the formation of the polymer **1**. Part of the one-dimensional chain structure and views of the crystal packing in compound **1** are shown in Figs. 1 and 2, respectively. The Cu(1), O(1) and N(2) atoms are on a crystallographic C_2 axis. The copper(I) atom is co-ordinated to the two nitrogen atoms of the two phz molecules and to the two oxygen atoms of the NO$_3^-$ anion, in a distorted tetrahedral geometry which is almost the same as in the monomer [Cu(phz)$_2$(NO$_3$)] (see above). The Cu–N distance of 1.976(2) Å is slightly longer than that of 1.956 Å (average) in [Cu(phz)$_2$(NO$_3$)], while the Cu–O distance of 2.360(3) Å is a little shorter [2.372 Å (average)]. Phenazine now acts as a link between the two copper atoms and the N–Cu–N′ angle of 147.1(1)° results in a one-dimensional zigzag chain structure along the *a* axis as shown in Fig. 2(*a*). Two phz molecules co-ordinated to the same copper atom are inclined to each other at a dihedral angle of 82.2°. As can be seen in Fig. 2(*b*), the phz molecules are stacked in the *b*-axis direction with an interplane distance of 3.47 Å, indicating a π–π interaction between the phz molecules. The structure of compound **1** thus consists of one-dimensional zigzag chains of copper atoms and phz molecules, interconnected through phz π–π interactions, resulting in a two-dimensional interaction.

Structure of Compound **2**.—Adding a solution of acridine in methanol to a solution containing copper(I) and phenazine causes the formation of a discrete complex **2**, in which the phenazine molecules are replaced by acridine molecules. Such a ligand-exchange reaction is reasonable as acridine (pK_b 8.42) is a stronger base than phenazine (pK_b 12.77).[14] The molecular structure and views of the crystal packing in compound **2** are shown in Figs. 3 and 4, respectively. The copper(I) ion is trigonally co-ordinated to the two nitrogen atoms of the

Table 2 Atomic coordinates for [{Cu(phz)(NO$_3$)}$_\infty$] **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.250 0	0	0.047 39(3)
O(1)	0.250 0	0	0.289 1(2)
O(2)	0.294 6(2)	0.163 9(6)	0.175 8(2)
N(1)	0.105 9(1)	0.021 5(5)	0.013 4(1)
N(2)	0.250 0	0	0.216 1(2)
C(1)	0.039 2(2)	0.175 1(6)	0.052 1(2)
C(2)	0.074 5(2)	0.367 3(6)	0.104 9(2)
C(3)	0.007 6(2)	0.518 9(7)	0.143 9(2)
C(4)	−0.099 2(2)	0.488 6(7)	0.133 3(2)
C(5)	−0.135 3(2)	0.311 1(6)	0.081 9(2)
C(6)	−0.068 2(2)	0.150 3(6)	0.038 6(2)

Table 4 Atomic coordinates for [{Cu$_2$(phz)(PFO$_3$)}$_\infty$] **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.708 66(8)	0.339 58(3)	0.504 5(1)
Cu(2)	0.687 06(8)	0.146 98(3)	0.499 6(1)
P(1)	0.841 6(2)	0.251 03(6)	1.077 5(2)
F(1)	1.060 7(4)	0.250 8(2)	1.197 2(6)
O(1)	0.813 0(5)	0.323 1(2)	0.936 8(6)
O(2)	0.776 5(6)	0.175 6(2)	0.896 7(6)
O(3)	0.788 3(5)	0.250 7(2)	1.345 8(6)
N(1)	0.579 1(5)	0.429 9(2)	0.479 5(7)
N(2)	0.568 1(5)	0.061 6(2)	0.219 6(7)
C(1)	0.773 8(6)	0.492 9(2)	0.244 6(9)
C(2)	0.635 3(5)	0.495 0(2)	0.379 2(8)
C(3)	0.442 9(5)	0.434 3(2)	0.598 1(8)
C(4)	0.377 0(6)	0.368 5(3)	0.702(1)
C(5)	0.240 6(6)	0.372 6(3)	0.823(1)
C(6)	0.166 1(6)	0.442 5(3)	0.851(1)
C(7)	0.775 5(6)	−0.020 4(3)	0.508 4(9)
C(8)	0.634 8(6)	−0.007 6(2)	0.248 8(8)
C(9)	0.430 9(6)	0.069 6(2)	−0.026 0(8)
C(10)	0.348 9(7)	0.140 2(3)	−0.065(1)
C(11)	0.212 3(7)	0.148 7(3)	−0.310(1)
C(12)	0.151 8(7)	0.088 8(3)	−0.537(1)

Table 3 Atomic coordinates for [{Cu(acr)$_2$(NO$_3$)}$_2$(phz)(H$_2$O)] **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.248 18(8)	0.229 00(6)	0.364 89(8)
O(1)	0.105 1(5)	0.318 0(3)	0.256 2(5)
O(2)	−0.014 7(6)	0.225 6(4)	0.350 6(6)
O(3)	−0.103 7(6)	0.320 9(5)	0.209 6(7)
O(4)	1.000 0	0.500 0	1.000 0
N(1)	0.203 0(4)	0.100 8(3)	0.229 1(5)
N(2)	0.387 8(5)	0.325 5(3)	0.518 1(5)
N(3)	−0.005 3(7)	0.287 4(5)	0.273 7(6)
N(4)	0.542 7(5)	0.085 2(4)	0.113 8(6)
C(1)	0.204 0(5)	0.103 5(4)	0.096 3(6)
C(2)	0.237 7(6)	0.197 1(5)	0.056 4(7)
C(3)	0.240 2(7)	0.201 4(6)	−0.076 3(8)
C(4)	0.206 4(7)	0.110 0(7)	−0.178 4(7)
C(5)	0.174 5(7)	0.019 2(6)	−0.144 1(7)
C(6)	0.171 0(6)	0.011 0(5)	−0.006 5(6)
C(7)	0.139 3(6)	−0.081 2(5)	0.033 6(7)
C(8)	0.138 6(6)	−0.085 1(5)	0.167 8(7)
C(9)	0.107 0(7)	−0.178 7(5)	0.217 2(9)
C(10)	0.107 6(7)	−0.177 5(6)	0.351(1)
C(11)	0.140 1(8)	−0.083 6(6)	0.445 9(8)
C(12)	0.170 3(7)	0.005 4(5)	0.405 3(7)
C(13)	0.170 9(6)	0.009 9(4)	0.265 8(6)
C(14)	0.361 0(6)	0.383 5(4)	0.621 3(5)
C(15)	0.230 2(7)	0.364 6(5)	0.633 9(6)
C(16)	0.200 7(7)	0.423 0(5)	0.735 8(7)
C(17)	0.301 0(8)	0.503 3(5)	0.834 3(7)
C(18)	0.427 0(7)	0.523 7(5)	0.825 8(6)
C(19)	0.463 9(7)	0.464 8(4)	0.720 6(6)
C(20)	0.588 6(6)	0.483 6(4)	0.708 6(6)
C(21)	0.620 1(6)	0.425 8(4)	0.607 0(6)
C(22)	0.749 7(7)	0.442 5(5)	0.588 5(7)
C(23)	0.774 9(7)	0.382 6(5)	0.486 5(8)
C(24)	0.672 6(7)	0.300 7(5)	0.393 7(7)
C(25)	0.547 8(6)	0.282 7(4)	0.405 2(6)
C(26)	0.514 3(6)	0.343 9(4)	0.509 6(6)
C(27)	0.470 5(8)	−0.126 2(7)	0.290 0(9)
C(28)	0.508 5(7)	−0.029 8(6)	0.268 5(7)
C(29)	0.505 3(6)	−0.011 1(5)	0.131 9(7)
C(30)	0.539 0(6)	0.096 4(5)	−0.016 1(7)
C(31)	0.579 0(7)	0.195 9(5)	−0.043 6(9)
C(32)	0.574 3(7)	0.211 3(6)	−0.174(1)

Table 5 Atomic coordinates for $[\{[Cu(phz)(MeCN)]_2(C_{16}H_{10})(PF_6)_2\}_\infty]$ **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.101 99(6)	0.241 47(4)	0.079 83(7)
P(1)	0.605 5(2)	0.147 6(1)	0.812 9(2)
F(1)	0.631 5(4)	0.061 6(3)	0.664 1(4)
F(2)	0.578 6(5)	0.235 5(3)	0.960 3(5)
F(3)	0.573 5(4)	0.239 1(3)	0.695 0(5)
F(4)	0.638 5(5)	0.057 5(3)	0.929 0(4)
F(5)	0.453 4(4)	0.139 0(3)	0.806 3(6)
F(6)	0.757 9(4)	0.160 9(4)	0.818 4(6)
N(1)	0.041 7(3)	0.390 5(3)	0.027 0(4)
N(2)	0.040 5(3)	0.100 7(2)	0.033 1(4)
N(3)	0.276 3(4)	0.204 3(3)	0.199 2(5)
C(1)	−0.086 9(4)	0.442 1(3)	0.050 9(5)
C(2)	0.129 1(4)	0.447 9(3)	−0.024 2(5)
C(3)	0.264 4(4)	0.398 6(3)	−0.054 8(6)
C(4)	0.351 8(4)	0.454 8(4)	−0.106 5(6)
C(5)	0.310 4(5)	0.564 2(4)	−0.127 7(6)
C(6)	−0.182 4(5)	0.385 2(3)	0.101 4(6)
C(7)	0.070 4(4)	0.038 9(3)	−0.105 8(5)
C(8)	−0.028 4(4)	0.061 7(3)	0.140 9(5)
C(9)	−0.059 8(5)	0.120 6(3)	0.292 4(6)
C(10)	−0.130 3(5)	0.083 3(4)	0.399 5(6)
C(11)	−0.175 9(5)	−0.015 6(4)	0.363 0(6)
C(12)	0.147 0(4)	0.074 2(3)	−0.222 2(6)
C(13)	0.383 6(6)	0.174 8(4)	0.240 7(6)
C(14)	0.521 0(6)	0.138 4(5)	0.295 9(7)
C(15)	0.223 1(7)	0.595 6(5)	0.369 7(7)
C(16)	0.326 8(6)	0.511 9(6)	0.396 2(7)
C(17)	0.303 6(6)	0.423 2(5)	0.464 8(7)
C(18)	0.173 3(5)	0.416 5(4)	0.505 8(6)
C(19)	0.067 4(5)	0.502 1(4)	0.479 3(5)
C(20)	0.092 5(6)	0.592 4(4)	0.409 9(6)
C(21)	−0.017 6(7)	0.677 9(4)	0.387 1(7)
C(22)	0.142 1(6)	0.324 8(4)	0.573 0(7)

Table 6 Selected bond distances (Å) and angles (°) for compounds **1**–**4**

	1	**2**	**4**
Cu(1)–N(1)	1.976(2)	1.955(4)	1.978(3)
Cu(1)–O(2)	2.360(3)	—	—
N(2)–O(1)	1.203(4)	—	—
N(2)–O(2)	1.240(3)	—	—
Cu(1)–O(1)	—	2.215(5)	—
Cu(1)–N(2)	—	1.946(5)	2.005(3)
Cu(1)–N(3)	—	—	1.973(4)

	3		
Cu(1)–O(1)	2.091(3)	Cu(1)–O(3′)[a]	1.928(3)
Cu(1)–N(1)	1.921(3)	Cu(2)–O(2)	1.891(3)
Cu(2)–O(3′)[a]	2.181(3)	Cu(2)–N(2)	1.913(3)
P(1)–O(1)	1.475(3)	P(1)–O(2)	1.493(3)
P(1)–O(3)	1.520(3)	P(1)–F(1)	1.581(3)
Cu(1) · · · Cu(2)	3.3413(8)		

	1		**2**
N(1)–Cu(1)–N(1′)[b]	147.1(1)	O(1)–Cu(1)–N(1)	102.8(2)
N(1)–Cu(1)–N(2)	106.4(1)	N(1)–Cu(1)–N(2)	146.4(2)
O(2)–Cu(1)–O(2′)[b]	52.6(1)	O(1)–Cu(1)–N(2)	106.9(2)
O(2)–N(2)–O(2′)[b]	115.1(4)	Cu(1)–O(1)–N(3)	107.5(4)

	3		
O(1)–Cu(1)–O(3′)[a]	99.7(1)	O(1)–Cu(1)–N(1)	106.4(1)
O(3′)[a]–Cu(1)–N(1)	153.7(1)	O(2)–Cu(2)–O(3′)[a]	100.7(1)
O(2)–Cu(2)–N(2)	142.6(1)	O(3′)[a]–Cu(2)–N(2)	116.4(1)
O(1)–P(1)–O(2)	118.2(2)	O(1)–P(1)–O(3)	114.1(2)
O(2)–P(1)–O(3)	111.7(2)	Cu(1)–O(1)–P(1)	130.3(2)
Cu(2)–O(2)–P(1)	134.1(2)	Cu(1)–O(3′)[a]–Cu(2)	108.7(1)
Cu(1)–O(3′)[a]–P(1)	122.9(2)	Cu(2)–O(3′)[a]–P(1)	124.4(2)

	4		
N(1)–Cu(1)–N(2)	137.8(1)	N(1)–Cu(1)–N(3)	118.7(2)
N(2)–Cu(1)–N(3)	103.3(1)	Cu(1)–N(3)–C(13)	167.5(4)

[a] Symmetry codes: $x, y, z - 1$. [b] Symmetry code: $\frac{1}{2} - x, -y, z$.

Table 7 Dihedral angles and interplane distances in compounds **1**–**4**

Compound	Molecules defining planes		Dihedral angle/°	Interplane distance/Å
1	phz[a]	phz[a]	82.2	—
	phz[b]	phz[b]	0	3.47
2	acr(1)	acr(1)	0	3.41
	acr(1)	phz	5.9	(3.39)[c]
	acr(1)	acr(2)	63.6	—
	acr(2)	acr(2)	0	3.49
3	phz(1)	phz(1)	0	3.43
	phz(2)	phz(2)	0	3.31
	phz(1)	phz(2)	85.2	—
4	phz(1)	pyrene	10.7	(3.37)[c]
	phz(2)	phz(2)	0	3.47
	phz(1)	phz(2)	59.4	—

[a] Co-ordinated to the same copper atom. [b] Forming a columnar stack. [c] The nearest C · · · C distance.

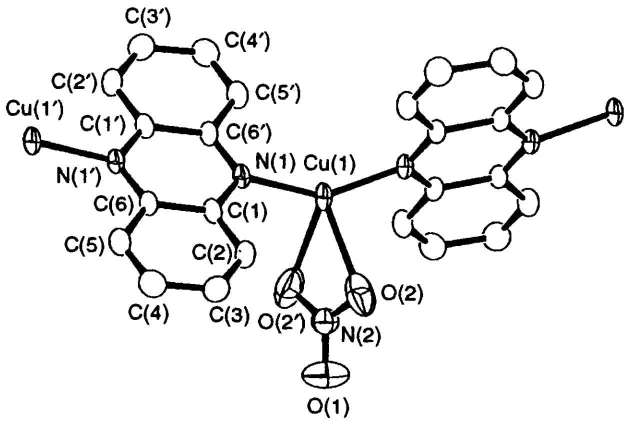


Fig. 1 ORTEP drawing of the asymmetric unit in the one-dimensional chain of $[\{Cu(phz)(NO_3)\}_\infty]$ **1** showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity

acridine and one of the oxygen atoms of the NO_3^- anion. The monodentate co-ordination of the NO_3^- anion is in clear contrast to the bidentate co-ordination in compound **1** and $[Cu(phz)_2(NO_3)]$. The shorter Cu–O distance of 2.215(5) Å in **2** compared to that in **1** or $[Cu(phz)_2(NO_3)]$ is reasonable. The average Cu–N distance of 1.950 Å is almost the same as that in $[Cu(phz)_2(NO_3)]$ (1.956 Å). The co-ordination geometry around the copper(I) atom is almost planar, the deviation of the copper atom from the plane defined by the co-ordinating atoms is *ca.* 0.21 Å. The T-shaped geometry is demonstrated by the large N(1)–Cu(1)–N(2) angle of 146.4(2)°. The middle Cu(1)–O(1) bond distance of 2.215(5) Å is longer than the two terminal bond distances of 1.955(4) and 1.946(5) Å as well as those in other T-shaped copper(I) compounds.[15,16] The two acridine molecules are not equivalent. The acridine molecule containing the N(1) atom and that containing the N(2) atom, called hereafter acr(1) and acr(2), respectively, are inclined towards each other at a dihedral angle of 63.6° and each has a π–π interaction with an adjacent acridine molecule co-ordinated to another copper atom (see Fig. 4). Interplane separations for the acr(1) and for the acr(2) molecules are 3.41 and 3.49 Å, respectively. Interestingly, a metal-free phenazine molecule is sandwiched between the acr(1) molecules forming an infinite columnar

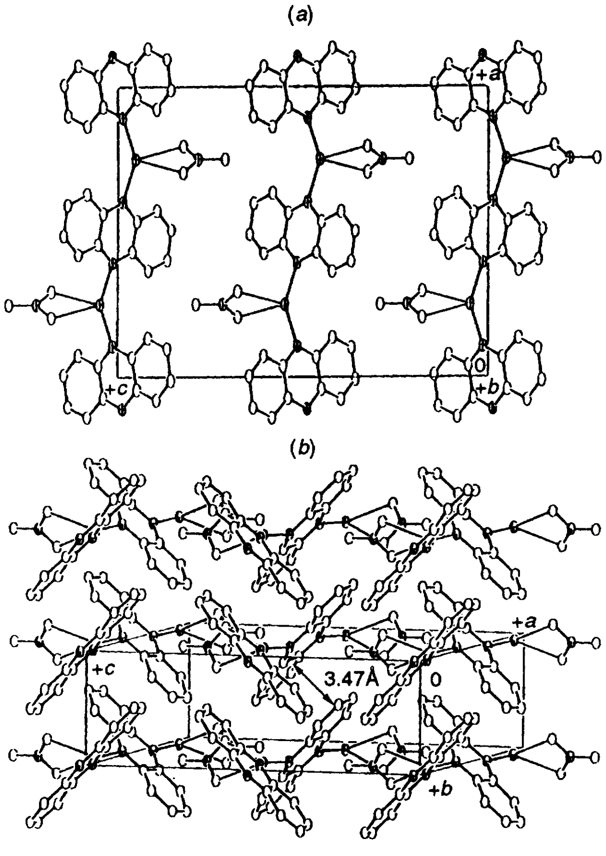


Fig. 2 Top (*a*) and side view (*b*) of the crystal packing of compound **1** showing the phenazine columnar stacks

stack along the *a* axis with a phz–acr–acr repeating unit. The phz plane is inclined a little (5.9°) to the acr plane. The closest C $\cdots$ C distance is 3.39(1) Å [C(5) $\cdots$ C(29′)], indicating a significant π–π interaction between the phenazine and acridine molecules. As can be seen from Fig. 4, a water molecule (an oxygen atom) is incorporated into the crystal, whose origin is probably the copper(II) nitrate trihydrate used as a starting material.

Structure of Compound **3**.—The asymmetric unit and views of the crystal packing in compound **3** are shown in Figs. 5 and 6, respectively. One of the remarkable features of this compound is that the copper atoms are bridged by two types of linking ligands, phenazine and the $\mathrm{PFO_3}^{2-}$ anion, alternately, forming a one-dimensional chain structure along the *b* axis. The bridging mode of the $\mathrm{PFO_3}^{2-}$ anion is quite unique: two of the three oxygen atoms bridge the two copper atoms Cu(1) and Cu(2) and the other oxygen atom [O(3)] bridges a pair of copper atoms residing in the neighbouring chain. The $\mathrm{PFO_3}^{2-}$ anion thus acts as a tetradentate bridging ligand, connecting adjacent one-dimensional chains, which results in a two-dimensional network structure spread in the *bc* plane. Two $\mathrm{PFO_3}^{2-}$ anions and two copper(I) ions form a six-membered ring. Both copper(I) ions have trigonal-planar, T-shaped geometry with co-ordination to a nitrogen atom from the phenazine and to two oxygen atoms from the two $\mathrm{PFO_3}^{2-}$ anions. Deviations of both copper atoms from their co-ordination planes are very small [0.033 for Cu(1) and 0.060 Å for Cu(2)]. The dihedral angle between these planes is 54.7°, indicating a large distortion in the six-membered ring. The T-shaped geometry of these copper(I) ions are demonstrated by the large O(3′)–Cu(1)–N(1) [153.7(1)°] and O(2)–Cu(2)–N(2) [142.6(1)°] angles compared to the other angles around these copper(I) ions. The middle bond distance of each T-shaped copper(I) ion is longer than the two terminal bond distances as

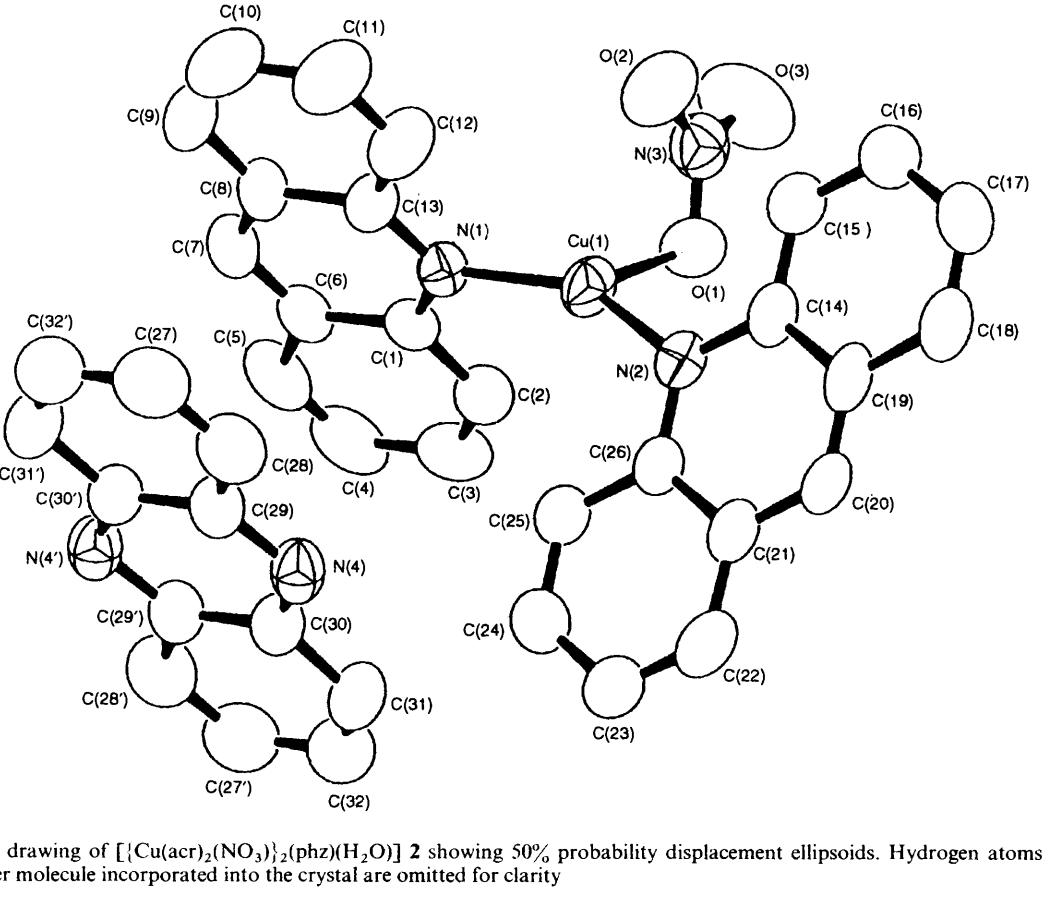
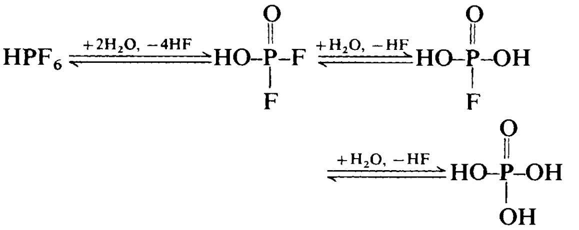


Fig. 3 ORTEP drawing of $[\{\mathrm{Cu(acr)_2(NO_3)}\}_2\mathrm{(phz)(H_2O)}]$ **2** showing 50% probability displacement ellipsoids. Hydrogen atoms and the O(4) atom of the water molecule incorporated into the crystal are omitted for clarity

well as those in other T-shaped copper(I) compounds,[16] including compound **2**. It should be noted that the bridging modes of the PFO_3^{2-} anion to the two pairs of copper atoms are both asymmetric. The Cu(1)–O(1) distance [2.091(3) Å] is longer than Cu(2)–O(2) [1.891(3) Å], while Cu(1)–O(3′) [1.928(3) Å] is shorter than Cu(2)–O(3′) [2.181(3) Å]. The average Cu–N distance of 1.917 Å is shorter than those of other three-co-ordinated copper(I) compounds excluding the T-shaped ones. The two phenazine molecules [phz(1) containing N(1) and phz(2) containing N(2)], depicted in Fig. 5, are inclined towards each other at a dihedral angle of 85.2° and are crystallographically non-equivalent. Both phz molecules form infinite stacks along the *c* axis with interplane separations of 3.43 and 3.31 Å for phz(1) and phz(2), respectively. The Cu(1) ⋯ Cu(2) distance is 3.3413(8) Å, indicating no direct interaction.

The origin of the PFO_3^{2-} anion is definitely the PF_6^- anion. It is well known that hydrolysis of hexafluorophosphoric acid gives several fluorine-substituted phosphoric acids step by step as in reaction (1).[17,18] The present X-ray result indicates that



$$\mathrm{HPF_6} \xrightleftharpoons{+2H_2O,\ -4HF} \mathrm{HO{-}P(=O)(F){-}F} \xrightleftharpoons{+H_2O,\ -HF} \mathrm{HO{-}P(=O)(F){-}OH} \xrightleftharpoons{+H_2O,\ -HF} \mathrm{HO{-}P(=O)(OH){-}OH} \quad (1)$$

hydrolysis takes place until the production of the PFO_3^{2-} anion. The origin of the water was probably an impurity in the acetone which could not be removed by the purification method mentioned above.

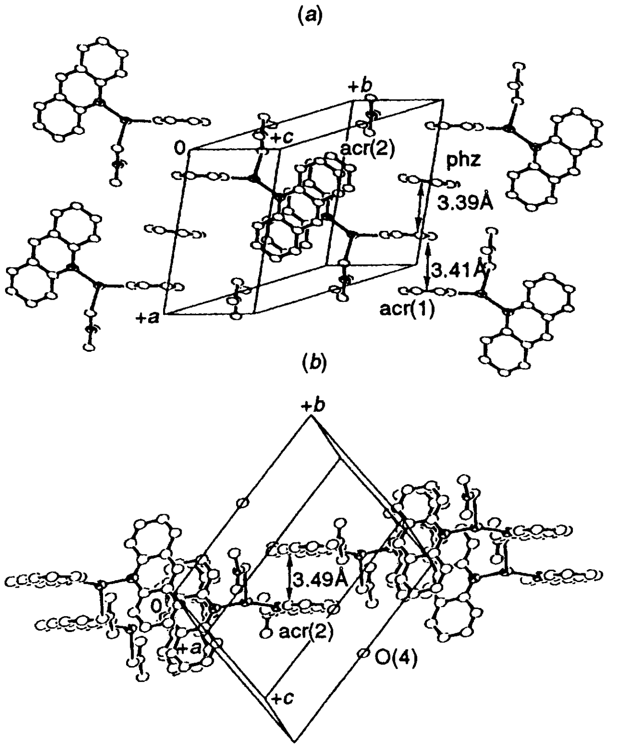


Fig. 4 Molecular views indicating π–π interaction between phz and acr(1) (*a*) and between acr(2) and acr(2) (*b*)

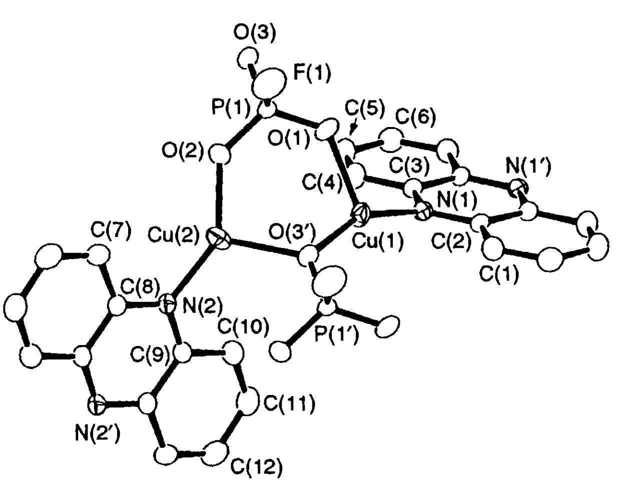


Fig. 5 ORTEP drawing of the asymmetric unit in $[\{Cu_2(phz)(PFO_3)\}_\infty]$ **3** showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity

Structure of Compound **4**.—Fig. 7 shows an asymmetric unit of compound **4**. The copper atom has trigonal-planar geometry with two nitrogen atoms from two phenazine molecules and one nitrogen atom from the acetonitrile. The average Cu–N(phz) distance of 1.992 Å is the longest one in this study. The deviation of the copper atom from the co-ordinating plane is only 0.044 Å. The backbone of this compound is similar to that of **1**: copper atoms are linked by phz molecules making an infinite zigzag chain structure along the direction of the *b* axis (Fig. 8). One of the characteristic features of this compound is that a pyrene molecule is incorporated into the crystal structure and is located near to a phz(1) molecule. Although these molecules are tilted a little to each other (dihedral angle 10.7°), the closest C ⋯ C separation of 3.368(7) Å for C(3) ⋯ C(22′) is short enough to indicate the existence of a π–π interaction between them. In the crystal

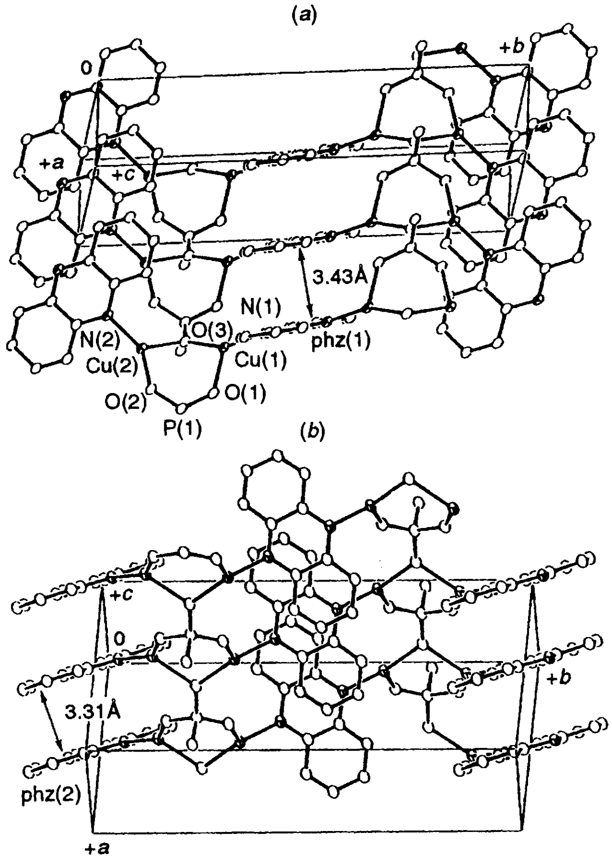


Fig. 6 Views of the crystal packing of compound **3** from the (−1,0,1) direction (*a*) and that rotated 90° from (*a*) around the *b* axis (*b*)

structure, these two molecules stack alternately along the direction of the *c* axis forming an infinite columnar stack (Fig. 8). On the other hand, phz(2) can also form an infinite columnar stack solely along the same direction because phz(1) and phz(2) are inclined towards each other with a dihedral angle of 59.4°. The interplane distance for the phz(2) stacking is 3.47 Å although the overlap is only restricted to the terminal C–C region.

Electrical Conductivity.—Powder or microcrystalline samples of compounds **3** and **5** were subjected to electrical conductivity measurements at room temperature. The highest conductivities obtained for **3** and **5** were $10^{-7.6}$ and $10^{-4.7}$ S cm^{-1} respectively. These values are within the semiconducting region. The other compounds show no measurable conductivity, indicating that they are insulators.

Discussion

Construction of One-dimensional Chain and Two-dimensional Sheet Structures with π–π Stacking.—Fig. 9 shows the schematic molecular packing of some copper(I) phenazine complexes. A co-ordination number of phenazine to copper(I) hitherto known is two or less.[8,9] This is also true for compounds in this study and leads to one-dimensional polymeric structures for the copper(I) phenazine skeleton in compounds **1** and **4**. For smaller linking ligands such as substituted pyrazines, three- or four-fold co-ordination of the ligands to copper(I) is observed,[19] which results in two- or three-dimensional network structures as expected.

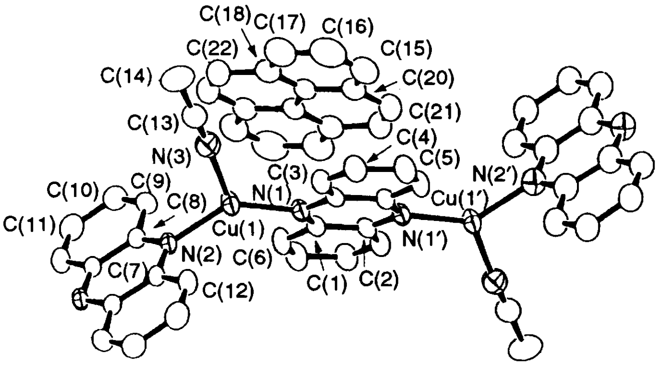


Fig. 7 ORTEP drawing of the asymmetric unit in [{[Cu(phz)(MeCN)]$_2$(C$_{16}$H$_{10}$)(PF$_6$)$_2$}$_\infty$] **4** showing 50% probability displacement ellipsoids. Hydrogen atoms and the PF$_6^-$ anions are omitted for clarity

A characteristic feature common to compounds **1**, **3** and **4** is the coexistence of a π–π phenazine stacking structure and a one-dimensional chain or two-dimensional sheet structure. Neighbouring one-dimensional chains in **1** or **4** are connected to each other through π–π interaction, phz–phz separations of 3.47 Å are not that short but indicate significant π–π interaction. On the other hand, **3** is constructed from one-dimensional chains which are interconnected through PFO$_3^{2-}$ bridges. The resulting two-dimensional sheet also contains π–π phenazine stacking, with phz ··· phz 3.31 Å the shortest separation in the

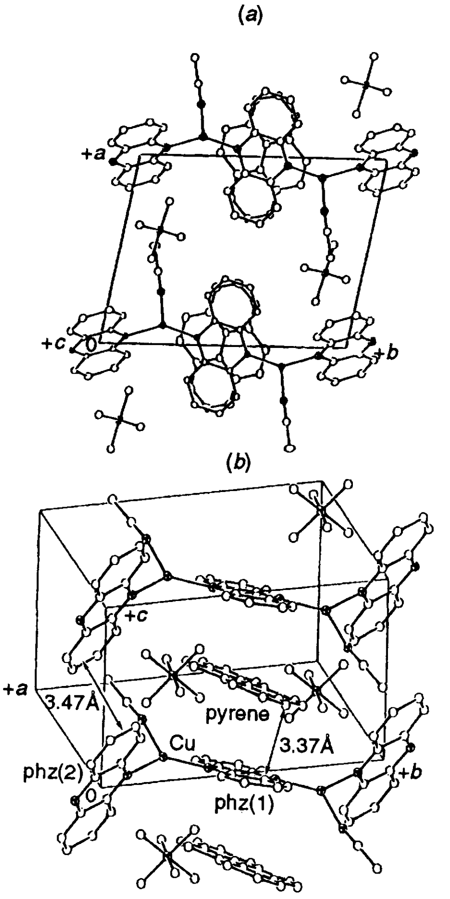
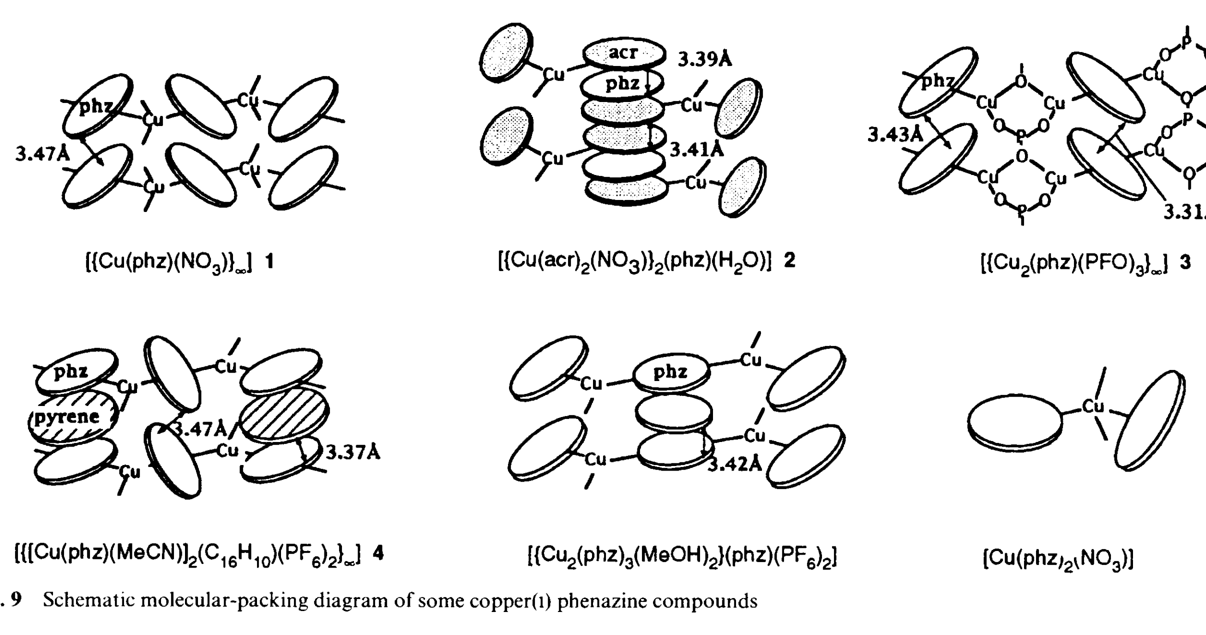


Fig. 8 View of the crystal packing from the *c* axis (*a*) and a side view of the pyrene–phenazine stacking (*b*) in compound **4**



[{Cu(phz)(NO$_3$)}$_\infty$] **1**

[{Cu(acr)$_2$(NO$_3$)}$_2$(phz)(H$_2$O)] **2**

[{Cu$_2$(phz)(PFO)$_3$}$_\infty$] **3**

[{[Cu(phz)(MeCN)]$_2$(C$_{16}$H$_{10}$)(PF$_6$)$_2$}$_\infty$] **4**

[{Cu$_2$(phz)$_3$(MeOH)$_2$}(phz)(PF$_6$)$_2$]

[Cu(phz)$_2$(NO$_3$)]

Fig. 9 Schematic molecular-packing diagram of some copper(I) phenazine compounds copper(I) or silver(I) phenazine compounds so far reported, indicating a strong π–π interaction. Probably some constraint caused by the bridging PFO_3^{2-} and/or crystal-packing forces results in the shortest separation. Such a structural constraint induces a perturbation on the electronic state of the compound, a perturbation which is thought to be responsible for the conducting property observed in **3** without iodine doping.

The most remarkable feature in compound **4** is the intercalation of pyrene molecules into a phenazine stack. Since the intercalation takes place between every other phenazine stack in the one-dimensional chain and the stack without intercalation is of course composed of phenazine molecules only, it is reasonable to consider that an iodine atom can easily penetrate the crystal. The relatively high conductivity of compound **5** indicates that partial oxidation of phenazine causes relatively high electron mobility of this compound.

Assignment of the Electronic Spectra of Copper Phenazine Compounds.—Two mononuclear compounds, **2** and $[Cu(phz)_2(NO_3)]$[9] (Fig. 9), show only one absorption at λ_{max} 500 and 460 nm, respectively, in the visible region. These are reasonably assigned to metal-to-ligand charge-transfer bands based on their similarity to those of copper(I) complexes with heteroaromatic nitrogen-donor ligands.[20] The corresponding λ_{max} absorption for compounds **1**, **3**, **4** and $[\{Cu_2(phz)_3(MeOH)_2\}(phz)(PF_6)_2]$[9] (Fig. 9) is observed at 560 nm. The significant red shift from 460 to 560 nm is reasonably understood to be due to the stabilization of the phenazine π* orbitals caused by double co-ordination to copper(I). In these compounds, an additional band is observed at 700 (**1** and **4**) or 710 nm (**3** and $[\{Cu_2(phz)_3(MeOH)_2\}(phz)(PF_6)_2]$. This *ca.* 700 nm band is also observed in other copper(I) phenazine co-ordination polymers with halogens, $[\{Cu_2(\mu\text{-}X)_2(\mu\text{-}phz)\}_\infty]$ (X = Cl, Br or I).[8] Since the common structural feature in these compounds is the existence of bridging phenazine, we can safely say that the *ca.* 700 nm band is characteristic of the Cu^I–phz–Cu^I structure.

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