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ARTICLE

A novel type of coordination mode of chloranilic acid leading to the formation of polymeric coordination ribbon in the series of mixed-ligand copper(II) complexes with 1,10-phenanthroline

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A series of four novel mixed-ligand complexes of copper(II) with 3,6-dichloro-2,6-dihydroxy-1,4-benzoquinone (chloranilic acid) and 1,10-phenanthroline was prepared and characterised by X-ray structure analysis and IR spectroscopy. Three complexes exhibit square-pyramidal coordination whereas one is in the octahedral coordination. The ligand 1,10-phenanthroline acts in a bidentate chelating mode with *N,N*-metal binding. Chloranilate dianion coordinates Cu^{II} atom in a terminal bidentate *ortho*-quinone-like mode forming mononuclear complex species. However, in one structure a novel type of coordination mode of chloranilate is observed. In addition to the bidentate mode, a monodentate bridging one through a carboxy oxygen of a symmetry related dianion leads to the formation of polymeric coordination ribbon. Crystal packing of penta-coordinated species in addition to hydrogen bonding involves less common stacking interactions of chelate rings with π -systems of the ligands.

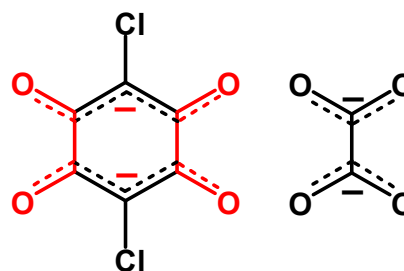
Introduction

Novel multifunctional materials based on conjugated π -electron systems have attracted a lot of attention in materials chemistry.¹⁻⁶ Out of these compounds, intensively studied are complexes of transition metals and organic π -functional ligands. It is well known that in the design of mono- and polynuclear (homo- and hetero-) complexes as potentially new functional materials with desirable physical properties (mechanical, optical, electrical, or magnetic), where an important role belongs to the oxalate C₂O₄²⁻ anion,⁷ being arguably one of the most versatile ligands. Its various possibilities of coordination to metal centres and the ability to mediate magnetic interactions between paramagnetic metal ions (separated by more than 5 Å) are responsible for the existence of a huge number of oxalate-based transition metal species, of different nuclearity and dimensionality.⁸⁻¹⁰ A recent use of oxalate complexes as precursors in synthesis of novel nanocrystalline mixed metallic oxides¹¹⁻¹³ has been widely exploited.

Thus, our recent (magneto)structural studies on the oxalate-based metal complexes¹⁴⁻¹⁷ have been extended on the reactions of the similar, but more stretched chloranilate dianion (Scheme 1) and transition metals. Our research is aimed to prepare novel (multi)functional materials using quinoid systems.¹⁸⁻²⁰ Proper

selection of mixed organic ligands to complex suitable metal ions should lead to desired architecture and properties. However, large number of compounds obtained during these syntheses, among which a limited number reveals desired properties, means that entirely controlled syntheses have not been reached, yet.

Chloranilate dianion ligand acts as a larger spacer, but still may allow some degree of charge transfer between the metal centres; it acts as an electron acceptor, and the interaction through its elongated conjugated π electron systems is feasible.



Scheme 1 Chloranilate dianion and an oxalate dianion with their analogous functional groups responsible for the coordination to metal ions.

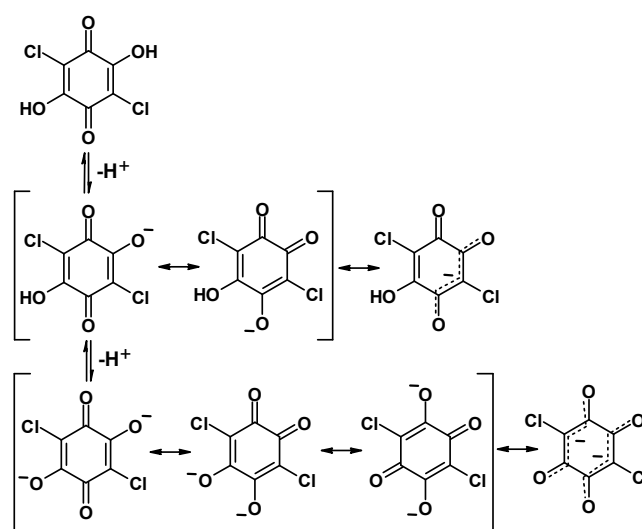
Our research has been directed to prepare and characterise mixed Cu^{II} complexes using 3,6-dichloro-2,6-dihydroxy-1,4-benzoquinone (chloranilic acid) and the nitrogen donor ligands

2,2'-bipyridine¹⁸ and its congener, 1,10-phenanthroline (in the present work). It is of interest to prepare mixed complex species to resolve an impact of binding mode of both ligands on metal coordination and crystal packing. In the series of Cu^{II} mixed complexes with chloranilic acid, coordinating in a terminal bidentate *ortho*-quinone-like mode, mononuclear species have been observed independently on using of 2,2'-bipyridine¹⁸ or 1,10-phenanthroline ligand. In the case of Cu^{II} complexes, an addition of bidentate chelating *N*-ligands, generally, favours the formation of mononuclear units¹⁸ (as confirmed by here presented results).

However, in the present series a novel coordination bonding mode of chloranilic acid leading to the formation of polymeric species is observed. Both ligands include π -systems that can be stacked influencing crystal packings. A striking example is the recently described preparation, structure and magnetic properties of stable 1,2,5[thiadiazolo][3,4-f][1,10-phenanthroline 1,1-dioxide] radical anion which combines the strong electron-withdrawing property of the thiadiazole dioxide moiety and the acceptor ability of the entire radical anion. The phenanthroline and thiadiazole dioxide moieties act as the ligands, which are responsible for multidimensional interactions.²¹

Selection of chloranilic acid and 1,10-phenanthroline for the syntheses of complexes was motivated by highly functionalised properties of both ligands. A variety of electrical and magnetic properties can be engineered by a simple combination of quinones, metals and other ancillary ligands.^{4,23} Electronic properties of conjugated systems can be modified, thus allowing a wide variety of electrical and magnetic properties. Among the most interesting candidates for synthesis of novel multifunctional materials are stable organic radicals,^{4,23} such as semiquinones. Their closed-shell relatives, quinones, often participate in charge transfer, since they are easily reduced into the radical form. The combination of paramagnetic metal centres and electron-accepting quinoid rings is particularly interesting and promising in synthesis of novel functional materials,^{1-3,5,6,24} particularly spintronics, that are in our focus.^{19,20,24}

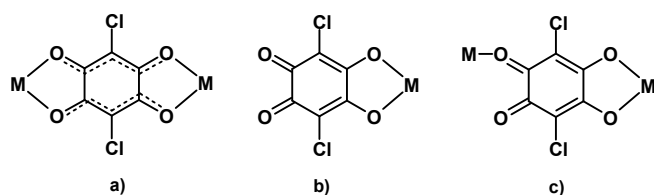
Substituted 2,5-dihydroxyquinones, such as chloranilic acid (3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone, CA, Scheme 2) are a sub-class of quinoid compounds which is especially promising for synthesis of novel functional materials. They are strong proton donors and acceptors²⁵ capable of forming various kinds of hydrogen bonds. Acidity of hydroxy-groups of 2,5-dihydroxyquinone is enhanced by electron-withdrawing substituents. Therefore, the unsubstituted 2,5-dihydroxyquinone behaves as a weak organic acid (with p*K*_a values of 2.73 and 5.18, respectively²⁶), but its dinitro analogue is a very strong acid comparable to the sulfuric or perchloric acid (its p*K*_a values being -3.0 and -0.5, respectively²⁶).



Scheme 2 Dissociation of chloranilic acid to the monoanion and dianion with resonance structures shown in brackets.

2,5-dihydroxyquinones are also good ligands and easily coordinate transition metals^{27,28}; they can act as bridging, (bis)bidentate or terminal, bidentate ligands (Scheme 3). The introduction of organic ligands containing *N*-donors influences the nuclearity and the topology of the metal centres and stabilizes the solid-state structures. Usually, 2,5-dihydroxyquinones behave as (bis)bidentate ligands with possibility to perform *catena*-bridging that generates polymeric complexes.²⁹⁻³⁷ However, mononuclear complexes with chloranilic acid acting as a terminal bidentate ligand are also known.^{18,33,34,38-40} Among polymeric species known³⁵ there is an example of the structure comprising chloranilate dianion and 1,10-phenanthroline ligands as we used to prepare complexes presented in this work. The bidentate chloranilate dianion acting as double bridging ligand generates a zig-zag polymeric eight-coordinated Cd(II) chains connected into 3D structure by stacking interactions between phen ligands arranged into offset face-to-face fashion.

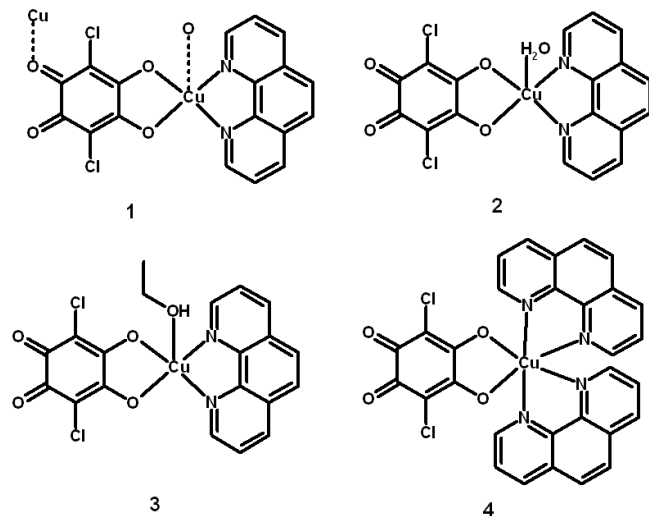
The self-assemblies of metal complexes with organic ligands, and sometimes solvents or guest molecules, based on combinations of intramolecular and intermolecular interactions reveal various topologies. Architectures such as chains, ladders, grids, honeycombs and others can be obtained forming voids shaped as cavities, channels and space between layers. Differently shaped space among the molecules and atoms, termed as nano-space can be functionalized for various purposes.²⁸



Scheme 3 Three coordination modes of chloranilic acid: a) bridging (bis)bidentate is the most common, but not observed in the series studied; b) terminal bidentate is less common, but observed in this study; and c) the novel bidendate + bridging monodendate mode observed for the first time in this study and leads to the formation of polynuclear species.

1,10-Phenanthroline has been widely exploited as a versatile ligand due to its distinctive properties.⁴¹ The rigid structure with the central aromatic ring keeps the two nitrogen in juxtaposition in contrast to 2,2'-bipyridine where a free rotation about the linking bond is possible. However, size of the two ligands is similar, so their analogous complexes may in some cases be isostructural.¹⁷ Due to the entropic advantage 1,10-phenanthroline easily makes metal complexes. An introduction of hydrophobic and bulky ligands into complexes is verified to be an effective way to enhance their stability, whereas their bulkiness reduce intermolecular interactions and can be of benefit for photoluminescence and electroluminescence. Thus, a plethora of metal complexes containing N,N' -chelating heterocycles including 1,10-phenanthroline have been used as functionalised molecules in optical devices,⁴² catalysis⁴³ and as components of supramolecular structures.⁴⁴ On the other hand, the ligand planarity make 1,10-phenanthroline to act as intercalating or groove-binding species with DNA and RNA,^{45,46} and also as nucleoside constituent for incorporation into the DNA backbone.⁴⁷

In this paper we report on a series of mononuclear complexes of chloranilic acid (its anion abbreviated as CA) and 1,10-phenanthroline (abbreviated as phen) with copper(II) (Scheme 4). A novel, bidendate + bridging coordination mode of chloranilic acid is described (Scheme 3c) which has been observed for the first time.

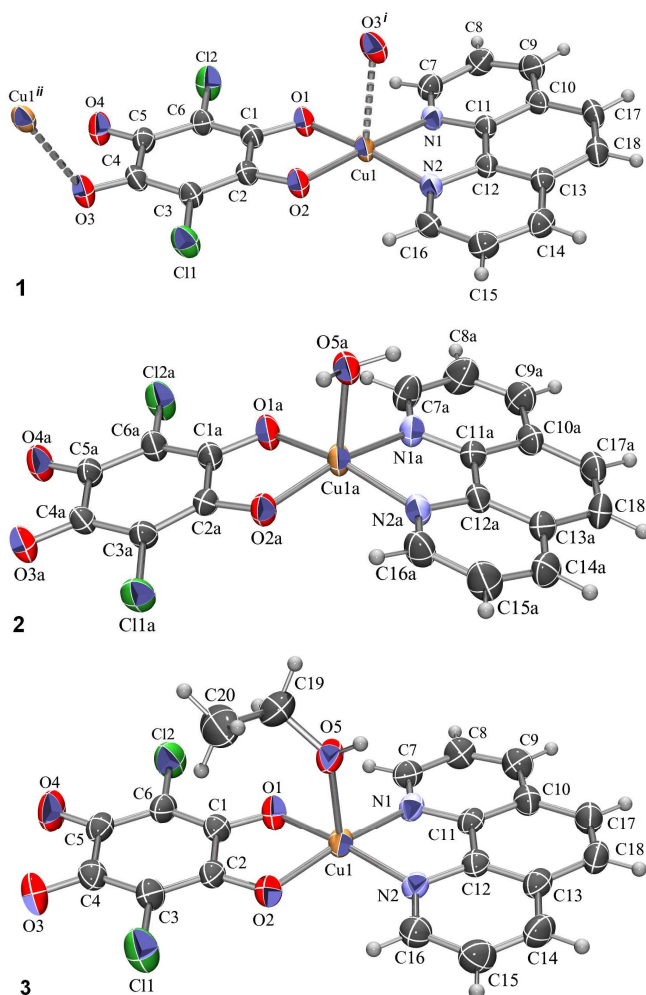


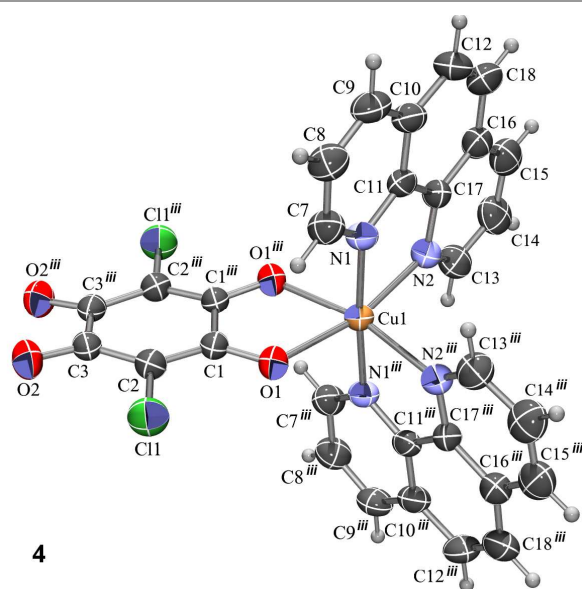
Scheme 4 Complexes described in this paper.

Results and discussion

Molecular structures

The novel mixed-ligand copper(II) complexes were prepared: $[\text{Cu}(\text{CA})(\text{phen})]_n$, (**1**), $[\text{Cu}(\text{CA})(\text{phen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (**2**), $[\text{Cu}(\text{CA})(\text{phen})(\text{C}_2\text{H}_5\text{OH})]$, (**3**), all three in the square-pyramidal coordination, and $[\text{Cu}(\text{CA})(\text{phen})_2]\cdot\text{CH}_3\text{OH}$, (**4**) with an octahedral coordination (Fig. 1, Table 1). The mononuclear complexes are encountered in **2**, **3** and **4**, whereas **1** is a polynuclear species. Their crystal structures and infrared spectroscopic characteristics are described.





4

Figure 1 Penta and hexa-coordinated complexes of: $[\text{Cu}(\text{CA})(\text{phen})]_n$, **1**, $[\text{Cu}(\text{CA})(\text{phen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, **2** (molecule **a**), $[\text{Cu}(\text{CA})(\text{phen})(\text{C}_2\text{H}_5\text{OH})]$, **3**, and $[\text{Cu}(\text{CA})(\text{phen})_2]\cdot\text{CH}_3\text{OH}$, **4**. Displacement ellipsoids are drawn at the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii. Symmetry operators: *i*) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; *ii*) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; *iii*) $1-x, y, \frac{1}{2}-z$.

The bite angles of bidentate phen and chloranilate ligands are considerably less than 90° (Table 1) significantly contributing to the coordination polyhedra distortion. The compound $[\text{Cu}(\text{CA})(\text{phen})]_n$ (**1**) comprises chloranilate (*O,O*) and phen ligands (*N,N*) coordinated to Cu in an equatorial plane (Fig. 1) with an additional O3 atom (from a symmetry related chloranilate dianion: $1-x, \frac{1}{2}+y, \frac{1}{2}-z$) located at an apical site of a square-pyramid. This bridging ligand generates a polymeric coordination chain. The observed Cu-O3 distance of 2.574(2) Å (Table 1) is significantly longer than the typical Cu-O covalent bond (1.98 Å), but it is shorter than the sum of van der Waals radii (2.92 Å⁴⁸). According to Cambridge Structural Database⁴⁹ distribution of Cu-O bonds is bimodal, with the average values at 1.95(4) Å and 2.36(16) Å; the larger value corresponds to longer distances observed in 4+1 and 4+2 coordinations, which are often longer than 2.5 Å. These coordination modes were recognised from structural and spectroscopic data^{33,50-52}. Penta-coordination mode in Cu^{II} complexes reveals square-pyramidal and trigonal-bipyramidal coordinations. The square planar, four-coordination, typical of d^9 configuration in Cu^{II} complexes is of high kinetic stability in comparison with penta-coordination.⁵³ The phen ligand is slightly twisted out of the equatorial plane with Cremer-Pople⁵⁴ puckering parameter $Q = 0.176(3)$ Å.

In $[\text{Cu}(\text{CA})(\text{phen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (**2**) and $[\text{Cu}(\text{CA})(\text{phen})(\text{C}_2\text{H}_5\text{OH})]$ (**3**) water and ethanol molecules are coordinated at the apical position of the square-pyramid (Fig. 1). Phen ligands in **2** are slightly twisted (with puckering amplitudes⁵⁴ being 0.159(3) and 0.086(3) Å for molecules **a** and **b**, respectively) and the angle between mean planes of chloranilate and phen ligands are 18.7° and 19.2° , respectively. However, **3** is more planar, with mean planes of phen and chloranilate being

inclined by only 1.0° ; puckering amplitude of phen is 0.209(7) Å. Copper atom is displaced by 0.129 Å above the least-squares plane of phen and CA ligands.

In $[\text{Cu}(\text{CA})(\text{phen})_2]\cdot\text{CH}_3\text{OH}$ (**4**) two phen ligands are coordinated to the Cu^{II}, in an octahedral arrangement together with the ligand CA (Fig. 1) revealing the molecular symmetry C_2 . The octahedron is significantly distorted due to O-Cu-O and N-Cu-N bite angles, which are considerably smaller than 90° (Table 1).

Geometry of the chloranilate ligand (Table 2) is somewhere between a dianion and an *o*-quinone (Scheme 2), as found in similar mononuclear complexes with bpy as the ancillary ligand¹⁸ and it appears to be usual when a 2,5-dihydroxyquinone acts as a terminal bidentate ligand.²⁵ There are two sets of C-O bonds: those coordinated to Cu are longer (being close to single bonds, Table 2), while uncoordinated ones are shorter (being close to double bonds, Table 2). The *o*-quinoid electronic structure is also confirmed by IR spectroscopy (Table 3).

Selected absorption bands ascribed to the vibrations of bidentate chloranilate anion for compounds **1–4** are given in Table 3.⁵⁵ The red and blue shifts of the observed position of the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{C})$, respectively, relative to the infrared spectra of solid chloranilic acid (H_2CA),⁵⁶ are due to the existence of delocalization in the terminal bidentate chloranilate anion in compounds **1–4**. Two peaks of very low intensity at 1629 and 1611 cm^{-1} present in the spectrum of compound **1** could be ascribed to the binding of one of the C=O bonds of chloranilate dianion to the copper(II) atoms in a bridging mode leading to the formation of the polymeric ribbon. Other absorption bands of the significant intensity in the spectra of compounds **1–4** correspond to different vibrations of the 1,10-phenanthroline ligand.⁵⁷

The broad band of strong intensity with the maximum around 3420 cm^{-1} in the spectrum of compound **2** originates from the O–H stretching vibration [$\nu(\text{OH})$] and are in agreement with the presence of the coordinated and crystal water molecules. The relatively sharp bands of medium intensity centred at 3394 cm^{-1} in the spectra of **3** and **4** are consistent with the O–H stretching vibration [$\nu(\text{OH})$] of alcohol solvates involved in the intermolecular hydrogen bonds.⁵⁵

Crystal packing

In the series studied penta-coordinated complexes crystalized in the noncentrosymmetric space groups whereas octahedral complex reveals the molecular symmetry C_2 with Cu^{II} located on a twofold rotation axis in the space group $C2/c$. The topology of their packing patterns is entirely different (Figs. 2–7). The two types of interactions occur in their crystal packing; hydrogen bonding occurs in **3** and **4** whereas in **1** stacking interactions are encountered, only. However, crystal packing of **2** reveals intensive interactions of both types (Tables 4 and 5). In **3** intramolecular interactions are represented also by both types including hydrogen bond between ethanol molecule and chloranilate, and phen...chloranilate stacking interaction (Tables 4 and 5). In the complexes **2** and **3** with ligands having

proton donor and acceptor functionalities, hydrogen bonding interactions affect their crystal packing (Table 5, Figs. 4-6). The crystal solvent molecules in **2** and **4** play a role in their crystal packing (Table 5) via formation of hydrogen bonds (Table 5). Due to a lack of proton donor/acceptor functionalities in **1**, hydrogen bonding is not possible. However, crystal packing of **1** is dominated by stacks of a) Cu-O-chloranilate chelate rings with phen rings, b) Cu-N-chelate-phen rings with phen rings (Fig. 8), and c) chloranilate...phen rings (Table 4, Figs. 3 and 8). An electron delocalization occurring in the five-membered Cu-chelate rings make them susceptible to interactions with other π -systems in the unit cell.⁵⁸⁻⁶² Direct stacks between chelate rings are not encountered in this series of complexes. On the contrary, such interactions were observed in the structures of mixed Cu(II) complexes with bipyridine and chloranilate.¹⁸

Chemically different rings being stacked in the complexes **1** – **3** are matched (details in Table 4): a) chelate ring...phen, b) chelate ring...chloranilate, c) chloranilate...phen, and d) phen...phen are arranged in nearly parallel arrangement with the tilt angle in the range 0.63(14)-19.86(11)°. The offset between rings is observed in the crystal packing of **2** and **3**, whereas in **1** there is no offset, at all. Geometrical parameters point out to the presence of specific interactions in the crystal packing of these complexes. However, an evaluation of their nature and the appropriate terminology are open to discussion.^{20,63,64}

The compound **1** reveals polymeric coordination chain of [Cu(CA)(phen)] units linked by the long Cu-O3ⁱ [symmetry operator *i*] 1-*x*, 1/2+*y*, 1/2-*z*] bond extending in the direction [010] (Fig. 2). Lacking proton donor sites, these chains are stacked through interactions of various π -systems, forming layers parallel to the plane (110) (Fig. 3, Table 4). There are dispersion interactions between these layers, only.

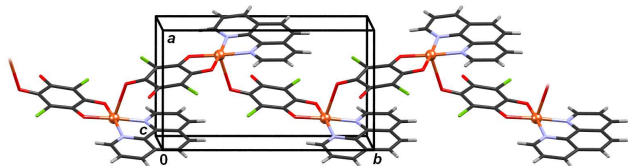


Figure 2 A polymeric ribbon of **1** extending in the direction [010].

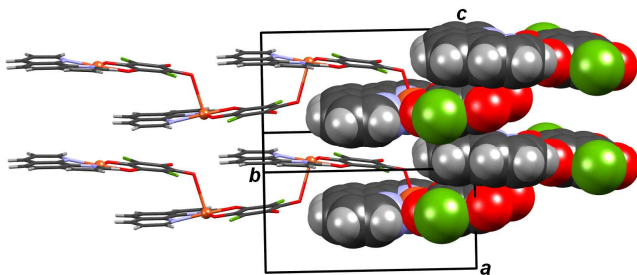


Figure 3 π -interactions between two contiguous coordination polymers of **1** reveal stacking of 1,10-phenanthroline and chloranilate moieties. To emphasize the stacking, a pair of [Cu(CA)(phen)] units has been depicted as van der Waals spheres.

In the crystal structure of **2** there are two symmetry-independent molecules, **a** and **b**, and a molecule of crystal water. The coordinated water molecule (O5) at the apical position of the square-pyramid acts as a donor of two protons in hydrogen bond, forming ladder-like double chains (**a** and **b** molecules) extending in the direction [100] (Fig. 4, Table 5). The crystal water molecule acts as a single proton donor in hydrogen bond as a pendant to molecule **b** (Fig. 4). In the crystal packing of **2** an extensive hydrogen bonding together with various combinations of π -interactions involving chelate, aromatic (phen), and quinoid (chloranilate) rings between chains, connect them into layers parallel to the plane (101) (Fig. 5). However, these layers are connected by dispersion interactions, only.

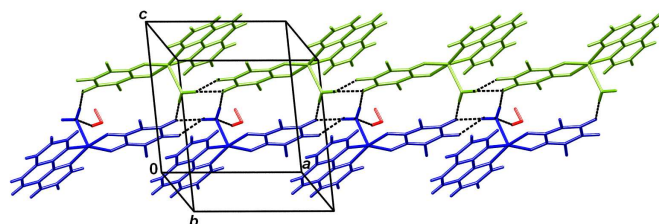
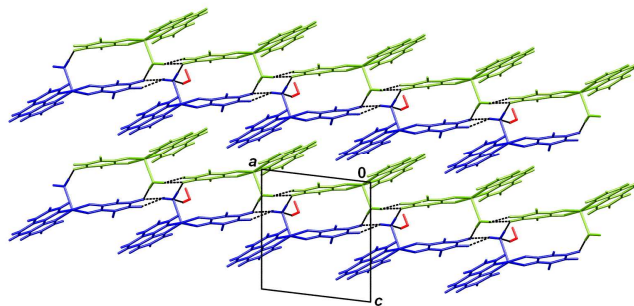


Figure 4 Crystal packing of **2** composed of hydrogen bonded chains of the two symmetry-independent molecules **a** (green) and **b** (blue).

The molecular structure of **3** reveals the coordinated ethanol molecule, located in the apical position, acting as a proton donor in hydrogen bond; chains formed extend in the direction [100] (Figure 6, Table 5). There is π -stacking between chloranilate and phen ligands (Table 4). Generally, dispersion interactions dominate in crystal structure of **3**.



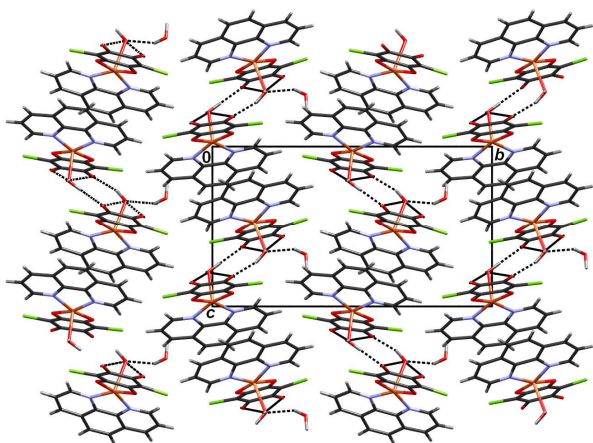


Figure 5 a) Stacking of 1,10-phenanthroline ligands between hydrogen bonded chains in **2** generating layers parallel to the plane (101); b) packing of the layers viewed in the direction [100].

Compound **4** crystallizes as a methanol solvate. MeOH molecule is disordered, with its methyl group lying on the rotation twofold axis. The OH group is disordered over two positions (of 0.5 population parameter), and in both orientations it serves as a proton donor to an O2 (chloranilate) of the same asymmetric unit (Table 5). Molecules of the complex are linked by C-H \cdots O and C-H \cdots Cl hydrogen bonds (Table 5). The porous crystal packing reveals channels running parallel to [001] that are filled by disordered methanol molecules (Fig. 7).

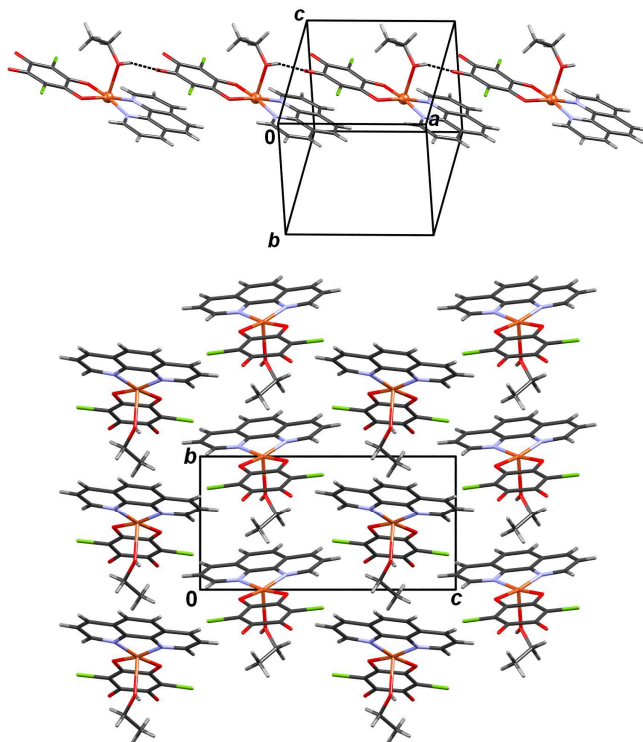


Figure 6 a) Hydrogen bonded chain of **3** parallel to [100]; b) packing of these chains viewed in the direction [100].

The five-membered Cu-*N,N*-phen and Cu-*O,O*-chloranilate chelate rings in **1** and **2** participate in stacking interactions with quinoid chloranilate and aromatic phenanthroline rings (Table 4). In both molecules (**a** and **b**) of asymmetric unit of **2**, Cu-*N*-phen and Cu-*O*-chloranilate chelate rings are planar [the average value of deviations from the least-square planes are: **a** 0.006(2), 0.007(2) Å; **b** 0.010(1), 0.013(2) Å, respectively] and prone for stacking with π -systems of ligands (Table 4). In contrast, in the series of Cu^{II} complexes comprising chloranilate and bpy ligands, chelate \cdots chelate stacks have been observed.¹⁸

There are quite a few examples of π -stacking between chelate and aromatic rings - the interactions are typically established by geometric criteria. Most typical examples are cyclopalladated azobenzenes⁶⁵⁻⁶⁷; recently we described the first examples of π -interactions between a chelate ring and a quinoid ring.¹⁸ However, these are more similar to aromatic stacks^{68,69} than quinoid stacks.^{19,70}

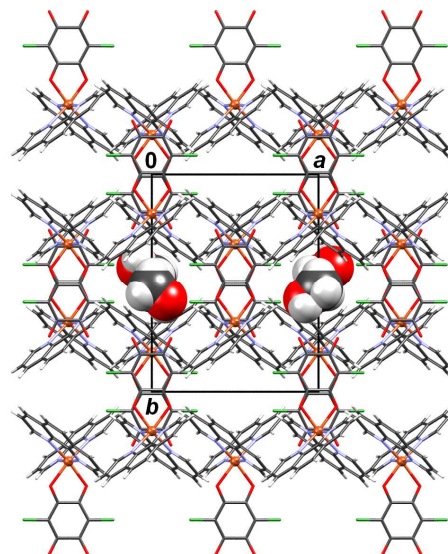


Figure 7 Crystal packing of **4** viewed in direction [001] with channels occupied by disordered MeOH molecules, presented by van der Waals spheres.

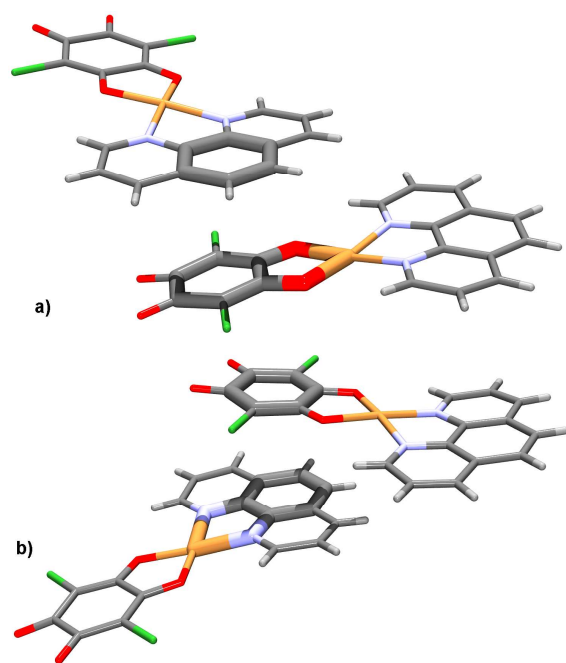


Figure 8 π -Interactions involving chelate rings in crystal packing of **1**: a) interaction of Cu-O-chelate ring with a phen ligand and b) interaction of Cu-N-chelate ring and chloranilate ligand.

Experimental

Materials and Physical Measurements The chemicals were purchased from commercial sources, and used without further purification. Infrared spectra were recorded by using KBr pellets with a Bruker Alpha FT-IR spectrometer, in the 4000–350 cm^{-1} region. Microanalysis was performed on a Perkin Elmer 2400 Series II CHNS/O Analyzer for compounds **2** and **3** (samples of other two compounds were inhomogenous due to presence of free chloranilic acid; however a few crystals could be separated to measure IR spectrum).

Preparation

Preparation of [Cu(CA)(phen)]_n (1**)** After mixing a methanol solution (4 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.1 mg; 0.1 mmol) with a methanol solution (4 mL) of 1,10-phenanthroline (19.9 mg; 0.1 mmol), reaction mixture became cloudy and a green precipitate immediately formed. It was removed by filtration and the clear solution was carefully laid above an aqueous solution (5 mL) of H_2CA (20.9 mg; 0.1 mmol) into a test tube. Deep dark violet, almost black, prismatic single crystals of **1** were formed after a few weeks. The yield was ~29 %.

IR data (KBr, cm^{-1}): $\tilde{\nu} = 1646$ (m), 1636 (w), 1629 (sh), 1615 (sh), 1611 (m), 1588 (w), 1550 (vs), 1518 (s), 1499 (vs), 1458 (w), 1427 (m), 1366 (s), 1343 (m), 1310 (m), 1254 (w), 1223 (w), 1209 (sh), 1144 (sh), 1110 (w), 1051 (sh), 997 (w), 875 (w), 843 (s), 775 (w), 742 (w), 722 (m), 668 (w), 653 (w), 604 (m), 573 (m), 435 (w), 419 (w).

Preparation of [Cu(CA)(phen)(H₂O)]·H₂O (2**)** After mixing an ethanol solution (4 mL) of 1,10-phenanthroline (19.9 mg;

0.1 mmol) with an ethanol solution (4 mL) of H_2CA (20.9 mg; 0.1 mmol), the clear solution was carefully laid above an aqueous solution (6 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.1 g; 0.1 mmol) into a test tube. X-ray quality black needle-like single crystals of **2** were formed after two weeks. The yield was ~78 %. Anal. Calcd. for $\text{C}_{36}\text{H}_{22}\text{Cl}_4\text{Cu}_2\text{N}_4\text{O}_{11}$ (Mr = 955.49): C 45.21, H 2.32, N 5.86%; found: C 45.47, H 2.22, N 5.86%.

IR data (KBr, cm^{-1}): $\tilde{\nu} = 3420$ (s, br), 1646 (m), 1637 (w), 1615 (m), 1589 (w), 1543 (vs), 1517 (vs), 1475 (sh), 1458 (w), 1429 (m), 1373 (s), 1344 (m), 1331 (w), 1312 (w), 1267 (w), 1255 (sh), 1224 (w), 1149 (w), 1110 (w), 1050 (w), 999 (w), 877 (w), 845 (s), 775 (w), 742 (w), 721 (m), 668 (w), 652 (w), 602 (m), 573 (m), 435 (w), 419 (w).

Preparation of [Cu(CA)(phen)(C₂H₅OH)] (3**)** An aqueous solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.7 mg; 0.1 mmol; 3 mL) and of 1,10-phenanthroline (19.9 g; 0.1 mmol; 3 mL) were mixed by heating. The resulting solution was put into a test tube. Then, an ethanol solution (8 mL) of H_2CA (21.0 mg; 0.1 mmol) was carefully laid above. X-ray quality dark violet needle-like single crystals of **3** were formed after two weeks. The yield was ~57 %.

Anal. Calcd. for $\text{C}_{18}\text{H}_8\text{Cl}_2\text{CuN}_2\text{O}_4$ (Mr = 450.72): C 47.96, H 2.85, N 5.64%; found: C 45.20, H 2.34, N 5.83%. IR data (KBr, cm^{-1}): $\tilde{\nu} = 3394$ (m, br), 1648 (m), 1632 (w), 1614 (m), 1587 (w), 1541 (vs), 1526 (s), 1515 (vs), 1431 (m), 1374 (s), 1346 (m), 1330 (m), 1312 (sh), 1266 (w), 1225 (w), 1210 (sh), 1160 (sh), 1149 (w), 1110 (w), 1049 (w), 999 (w), 878 (w), 845 (s), 774 (w), 741 (w), 721 (m), 668 (w), 652 (w), 598 (m), 574 (m), 520 (w), 434 (w), 420 (w).

Preparation of [Cu(CA)(phen)]·CH₃OH (4**)** A hot aqueous solution (3 mL) of 1,10-phenanthroline (19.9 mg; 0.1 mmol) was added to an aqueous solution (4 mL) of H_2CA (21.0 mg; 0.1 mmol), followed by the appearance of thin dark needles, that were removed by filtration. [As detected spectroscopically, thin crystals contain phenanthroline and H_2CA molecules, but the crystals were not of the quality needed for the X-ray analysis.] The resulting violet solution was layered with a methanol solution (8 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17.1 mg; 0.1 mmol) into a test tube. The reaction mixture was left to stand undisturbed for one week to yield X-ray quality dark violet needle-like crystals of **4**. The yield was ~10 %.

IR data (KBr, cm^{-1}): $\tilde{\nu} = 3394$ (m, br), 1647 (m), 1635 (w), 1614 (m), 1587 (w), 1541 (vs), 1526 (s), 1515 (vs), 1431 (m), 1374 (s), 1346 (m), 1330 (m), 1312 (sh), 1266 (w), 1225 (w), 1210 (sh), 1160 (sh), 1149 (w), 1110 (w), 1049 (w), 999 (w), 879 (w), 845 (s), 774 (w), 741 (w), 721 (m), 668 (w), 652 (w), 598 (m), 574 (m), 520 (w), 434 (w), 419 (w).

Crystallography

Single crystal measurements were performed on an Oxford Diffraction Xcalibur Nova R (microfocus Cu tube) at room temperature [293(2) K]. Only the symmetry-independent part of

the Ewald sphere was measured; no Friedel pairs were measured in the case of non-centrosymmetric crystals. Program package CrysAlis PRO⁷¹ was used for data reduction. The structures were solved using SHELXS97⁷² and refined with SHELXL97.⁷² Models were refined using the full-matrix least squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to C atoms were modelled as riding entities using the AFIX command, while those bound to O were located in difference Fourier maps and refined with the following restraints: geometry of water molecules was constrained to $d(\text{O-H}) = 0.95(2)$ Å; $d(\text{H}\cdots\text{H}) = 1.50(4)$ Å, and the hydroxyl group to $d(\text{O-H}) = 0.82(2)$ Å.

Methanol molecules in **4** are disordered, with the methyl carbon located on the twofold axis. Therefore, two sets of hydroxy groups and methyl hydrogen atoms exist, with p.p. 0.5. However, geometry of the methanol molecule is not realistic due to the disorder.

Molecular geometry calculations were performed by PLATON,⁷³ and molecular graphics were prepared using ORTEP-3,⁷⁴ and CCDC-Mercury.⁷⁵ Crystallographic and refinement data for the structures reported in this paper are shown in Table 6.

Supplementary crystallographic data for this paper can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). CCDC 973343-973346 contain the supplementary crystallographic data for this paper.

Conclusions

In mixed ligand complexes of Cu^{II} comprising chloranilate and phen ligands a square-pyramidal coordination is predominant one. In a single case an octahedral one is found. The *N,N*-ligand binding of phen is of significant impact on occurrence of mononuclear species. Chloranilate coordinates in a terminal bidentate *ortho*-quinone like mode also supporting the formation of mononuclear species. However, in addition to this predominant mode of coordination, a bridging monodentate mode of chloranilate is encountered in **1**; the long Cu-O bridging bond of 2.574(2) Å connects complex molecules into the polymeric coordination chain. Spectroscopic IR data are in a good agreement with the structures described.

The crystal packing of the structures described here is controlled by hydrogen bonding and π -interactions (Tables 4 and 5). Predominant π -interactions in **1** include those of five-membered chelate rings and π -systems of the ligands (of chloranilate and aromatic phen rings) in near face-to-face arrangement (no offset and very small tilt angles between stacked rings, Table 4). In the crystal packing of **4** the octahedra connected by hydrogen bonds built a porous network filled by disordered methanol solvate molecules.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Table 1 Geometric parameters of copper(II) coordination spheres (Å, °). Symmetry operators: *i*) 1-x, 1/2+y, 1/2-z; *ii*) 1-x, y, 1/2-z.

	1		2A	2B	3
Cu1 - O1	1.924(2)	Cu1 - O1	1.943(2)	1.9481(19)	1.940(4)
Cu1 - O2	1.9309(15)	Cu1 - O2	1.9577(19)	1.942(2)	1.948(4)
Cu1 - N1	1.9924(19)	Cu1 - N1	2.011(2)	1.986(2)	1.993(5)
Cu1 - N2	1.991(2)	Cu1 - N2	2.009(2)	1.997(2)	1.985(5)
Cu1 - O3 ^{<i>i</i>}	2.574(2)	Cu1 - O5	2.1980(18)	2.281(2)	2.275(5)
O1 - Cu1 - O2	85.12(8)	O1 - Cu1 - O2	84.24(8)	84.22(8)	84.00(17)
O1 - Cu1 - N2	173.20(9)	O1 - Cu1 - N2	165.54(9)	166.66(9)	170.8(2)
O1 - Cu1 - N1	96.19(8)	O1 - Cu1 - N1	93.93(9)	93.73(8)	95.02(18)
O1 - Cu1 - O3 ^{<i>i</i>}	95.32(8)	O1 - Cu1 - O5	101.68(8)	102.53(8)	94.6(2)
O2 - Cu1 - N2	94.95(8)	O2 - Cu1 - N2	95.85(9)	95.13(9)	96.99(18)
O2 - Cu1 - N1	177.21(9)	O2 - Cu1 - N1	166.11(8)	164.11(9)	170.9(2)
O2 - Cu1 - O3 ^{<i>i</i>}	97.09(8)	O2 - Cu1 - O5	98.10(8)	96.60(8)	91.4(2)
N2 - Cu1 - N1	83.45(8)	N1 - Cu1 - N2	82.51(9)	83.25(9)	82.55(18)
N2 - Cu1 - O3 ^{<i>i</i>}	91.42(8)	N1 - Cu1 - O5	95.76(8)	99.22(8)	97.67(19)
N1 - Cu1 - O3 ^{<i>i</i>}	85.25(8)	N2 - Cu1 - O5	92.64(8)	90.80(8)	94.5(2)
	4				
Cu1 - N1 ^{<i>ii</i>}	2.016(2)				
Cu1 - N1	2.016(2)				
Cu1 - N2	2.161(3)				
Cu1 - N2 ^{<i>ii</i>}	2.161(3)				
Cu1 - O1	2.161(2)				
Cu1 - O1 ^{<i>ii</i>}	2.161(2)				
N1 ^{<i>ii</i>} - Cu1 - N1	175.73(11)				
N1 ^{<i>ii</i>} - Cu1 - N2	80.10(10)				
N1 ^{<i>ii</i>} - Cu1 - N2 ^{<i>ii</i>}	97.05(10)				
N1 ^{<i>ii</i>} - Cu1 - O1	92.21(10)				
N1 ^{<i>ii</i>} - Cu1 - O1 ^{<i>ii</i>}	91.15(10)				
N1 - Cu1 - N2	97.05(10)				
N1 - Cu1 - N2 ^{<i>ii</i>}	80.10(10)				
N1 - Cu1 - O1	91.15(10)				
N1 - Cu1 - O1 ^{<i>ii</i>}	92.21(10)				
N2 - Cu1 - N2 ^{<i>ii</i>}	97.34(10)				
N2 - Cu1 - O1	93.88(9)				
N2 - Cu1 - O1 ^{<i>ii</i>}	166.52(9)				
N2 ^{<i>ii</i>} - Cu1 - O1	166.52(9)				
N2 ^{<i>ii</i>} - Cu1 - O1 ^{<i>ii</i>}	93.88(9)				
O1 - Cu1 - O1 ^{<i>ii</i>}	76.10(9)				

Table 2 Bond lengths in the chloranilate dianion (Å).

	1	2A	2B	3	4*
C1 - C2	1.509(4)	1.521(4)	1.513(4)	1.515(8)	1.547(4)
C2 - C3	1.378(3)	1.377(3)	1.370(4)	1.374(8)	1.373(4)
C3 - C4	1.415(3)	1.414(4)	1.425(4)	1.414(9)	1.412(4)
C4 - C5	1.563(4)	1.556(4)	1.556(4)	1.543(10)	1.547(4)
C5 - C6	1.431(4)	1.426(4)	1.416(4)	1.433(9)	1.412(4)
C6 - C1	1.364(4)	1.375(4)	1.381(4)	1.368(8)	1.373(4)
C1 - O1	1.286(3)	1.279(3)	1.275(3)	1.287(7)	1.265(4)
C2 - O2	1.284(3)	1.280(3)	1.281(3)	1.277(6)	1.265(4)
C4 - O3	1.234(3)	1.230(3)	1.230(4)	1.233(8)	1.229(4)
C5 - O4	1.215(3)	1.220(3)	1.237(3)	1.213(9)	1.229(4)
C3 - C11	1.743(3)	1.731(3)	1.730(3)	1.731(6)	1.744(4)
C6 - C13	1.734(3)	1.725(3)	1.726(3)	1.735(6)	1.744(4)

*Equivalent bonds; due to the molecular symmetry C_2 , labelling is different.

Table 3 Selected absorption bands (cm^{-1}) of the bidentate chloranilate dianion in the IR spectra of compounds 1–4

Compound	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{C})$	$\nu(\text{C}-\text{Cl})$	$\delta(\text{CC}=\text{O})$	C–Cl wagging
1	1646	1636, 1615 1629, 1611	1366	997	843	668	573
2	1646	1637, 1615	1373	999	845	668	573
3	1647	1635, 1614	1374	999	845	668	574
4	1648	1632, 1614	1374	999	845	668	574

Table 4 Geometric parameters of the π -interactions.

$\pi \cdots \pi$	$\text{Cg}^a \cdots \text{Cg} / \text{\AA}$	α^b	β^c	$\text{Cg} \cdots \text{plane}(\text{Cg}2) / \text{\AA}$	Offset/ \AA^d	Symm. op. on Cg2
1						
Cu1→O2⋯C10→C17	3.6893(13)	8.58(11)	24.05	3.1189(9)	-	$-x, -1/2+y, 1/2-z$
Cu1→N2⋯C1→C6	3.9022(13)	15.64(11)	28.19	2.9241(9)	-	$1-x, 1/2+y, 1/2-z$
N1→C11⋯C1→C6	3.4014(15)	9.14(12)	7.64	3.3446(11)	-	$1-x, 1/2+y, 1/2-z$
C1→C6⋯C10→C17	3.5506(14)	8.34(12)	19.67	3.3583(10)	-	$-x, -1/2+y, 1/2-z$
C1→C6⋯C10→C17	3.9498(14)	8.34(12)	33.59	3.3321(10)	-	$1-x, -1/2+y, 1/2-z$
2						
Cu1a→N2a⋯N1b→C11b	3.6353(14)	3.17(12)	18.33	3.4050(9)	1.14	$2-x, 1/2+y, 2-z$
Cu1a→N2a⋯C10b→C17b	3.6618(15)	2.06(12)	24.08	3.3947(8)	1.49	$2-x, 1/2+y, 2-z$
Cu1b→N2b⋯N2a→C16a	3.4676(15)	0.84(12)	14.17	3.3596(12)	0.85	$2-x, 1/2+y, 2-z$
Cu1b→O2b⋯C1a→C6a	3.8621(15)	18.47(12)	26.96	3.8104(10)	-	$-1+x, y, z$
Cu1b→N2b⋯C10a→C17a	3.8244(15)	3.86(11)	29.52	3.4429(11)	1.88	$2-x, 1/2+y, 2-z$
N1a→C11a⋯N1b→C11b	3.8612(17)	5.77(14)	26.96	3.1547(9)	-	$2-x, 1/2+y, 2-z$
N2a→C16a⋯N1b→C11b	3.7184(17)	1.12(14)	24.78	3.3460(12)	0.91	$2-x, 1/2+y, 2-z$
N2a→C16a⋯C10b→C17b	3.7500(16)	0.63(14)	26.49	3.3745(12)	1.67	$2-x, 1/2+y, 2-z$
C10a→C17a⋯N1b→C11b	3.6922(16)	4.14(13)	20.02	3.4613(11)	1.26	$2-x, 1/2+y, 2-z$
3						
C1→C6⋯C10→C17	3.477(4)	2.1(3)	8.49	3.420(3)	0.51	$-1+x, y, z$

^a Cg = centre of gravity of the interacting

ring.

^b α = angle between planes of two interacting rings.

^c β = angle between Cg⋯Cg line and normal to the plane of the first interacting ring.

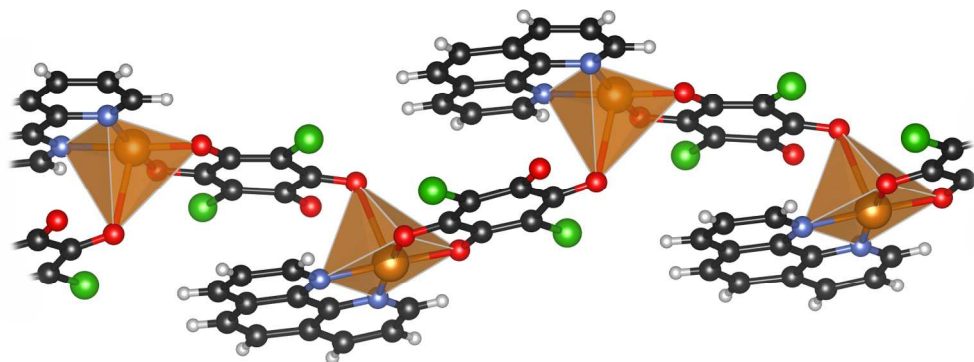
^d Offset can be calculated only for the strictly parallel rings ($\alpha = 0.00^\circ$). For slightly inclined rings ($\alpha \leq 5^\circ$) an approximate value is given.

Table 5 Geometric parameters of hydrogen bonds.

	<i>D</i> – <i>H</i> / Å	<i>H</i> ⋯ <i>A</i> / Å	<i>D</i> ⋯ <i>A</i> / Å	<i>D</i> – <i>H</i> ⋯ <i>A</i> / °	Symm. op. on <i>A</i>
2					
O5A–H5A⋯O4B	0.92(3)	1.86(3)	2.777(3)	176(3)	1– <i>x</i> , 1/2+ <i>y</i> , 1– <i>z</i>
O5A–H5B⋯O3A	0.93(2)	2.29(4)	3.018(3)	135(4)	1+ <i>x</i> , <i>y</i> , <i>z</i>
O5A–H5B⋯O4A	0.93(2)	2.04(4)	2.852(3)	135(4)	1+ <i>x</i> , <i>y</i> , <i>z</i>
O5B–H5C⋯O3A	0.83(4)	2.06(4)	2.841(5)	158(5)	<i>x</i> , <i>y</i> , <i>z</i>
O5B–H5D⋯O3B	0.93(3)	1.86(4)	2.755(3)	161(3)	1– <i>x</i> , –1/2+ <i>y</i> , 1– <i>z</i>
O5B–H5D⋯O4B	0.94(2)	2.19(5)	2.983(3)	143(6)	1+ <i>x</i> , <i>y</i> , <i>z</i>
O6–H6B⋯O5B	0.97(9)	2.06(9)	2.958(5)	152(6)	<i>x</i> , <i>y</i> , <i>z</i>
3					
O5–H5⋯O4	0.82(4)	2.06(5)	2.844(7)	161(6)	1+ <i>x</i> , <i>y</i> , <i>z</i>
O5–H5⋯O3	0.82(4)	2.46(5)	2.939(7)	118(6)	1+ <i>x</i> , <i>y</i> , <i>z</i>
4					
O3–H3⋯O2	0.82	2.31	2.764(8)	115	<i>x</i> , <i>y</i> , <i>z</i>
C7–H7⋯O3	0.93	2.77	3.247(9)	121	3/2– <i>x</i> , –1/2+ <i>y</i> , 1/2– <i>z</i>
C9–H9⋯O2	0.93	2.61	3.473(7)	154	<i>x</i> , 1– <i>y</i> , –1/2+ <i>z</i>
C9–H9⋯Cl1	0.93	2.91	3.643(8)	136	<i>x</i> , 1– <i>y</i> , –1/2+ <i>z</i>
C13–H13⋯Cl1	0.93	2.92	3.662(7)	138	3/2– <i>x</i> , –1/2+ <i>y</i> , 1/2– <i>z</i>

Table 6 Crystallographic, data collection and structure refinement details.

Compound	1	2	3	4
Empirical formula	C ₁₈ H ₈ Cl ₂ CuN ₂ O ₄	C ₃₆ H ₂₂ Cl ₄ Cu ₂ N ₄ O ₁₁	C ₂₀ H ₁₄ Cl ₂ CuN ₂ O ₅	C ₃ H ₃₀ Cl ₂ CuN ₄ O ₅
Formula wt. / g mol ^{–1}	450.72	955.49	496.79	662.98
Crystal dimensions / mm	0.25 x 0.12 x 0.07	0.20 x 0.18 x 0.02	0.22 x 0.10 x 0.05	0.16 x 0.10 x 0.06
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>
<i>a</i> / Å	7.44480(10)	9.53230(10)	9.00760(10)	12.3532(6)
<i>b</i> / Å	13.1466(2)	18.0066(2)	7.42350(10)	15.0096(7)
<i>c</i> / Å	16.0004(3)	10.39350(10)	14.1624(2)	16.3027(8)
<i>α</i> / °	90	90	90	90
<i>β</i> / °	90	96.8220(10)	90.8730(10)	111.011(6)
<i>γ</i> / °	90	90	90	90
<i>Z</i>	4	2	2	4
<i>V</i> / Å ³	1566.02(4)	1771.35(3)	946.90(2)	2821.8(2)
<i>D</i> _{calc} / g cm ^{–3}	1.912	1.791	1.742	1.561
<i>μ</i> / mm ^{–1}	5.399	4.876	4.567	3.255
θ range / °	4.35 – 75.74	4.28 – 75.75	3.12 – 75.80	4.84 – 75.75
<i>T</i> / K	293(2)	293(2)	293(2)	293(2)
Radiation wavelength	1.54179 (CuKα)	1.54179 (CuKα)	1.54179 (CuKα)	1.54179 (CuKα)
Diffractometer type	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova
Range of <i>h</i> , <i>k</i> , <i>l</i>	–9 < <i>h</i> < 6; –9 < <i>k</i> < 16; –19 < <i>l</i> < 17	–11 < <i>h</i> < 7; –22 < <i>k</i> < 19; –13 < <i>l</i> < 12	–6 < <i>h</i> < 11; –9 < <i>k</i> < 8; –17 < <i>l</i> < 17	–15 < <i>h</i> < 15; –16 < <i>k</i> < 18; –20 < <i>l</i> < 16
Reflections collected	4842	8683	4733	6044
Independent reflections	2853	5400	2775	2815
Observed reflections (<i>I</i> ≥ 2σ)	2771	5287	2724	2417
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
<i>R</i> _{int}	0.0211	0.0215	0.0212	0.0448
<i>R</i> (<i>F</i>)	0.0303	0.0273	0.0724	0.0467
<i>R</i> _w (<i>F</i> ²)	0.0807	0.0716	0.1997	0.1510
Goodness of fit	1.057	1.071	1.137	1.132
H atom treatment	Constrained	Mixed	Mixed	Mixed
No. of parameters	245	534	276	207
No. of restraints	0	11	3	9
Δρ _{max} , Δρ _{min} (eÅ ^{–3})	0.403; –0.392	0.425; –0.453	1.219; –1.177	0.526; –0.637



640x241mm (71 x 71 DPI)