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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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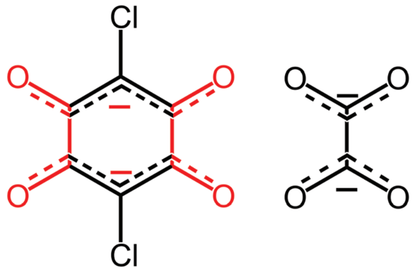
A series of four novel mixed-ligand complexes of copper(II) with 3,6-dichloro-2,6-dihydroxy-1,4-benzoquinone (chloranilic acid) and 1,10-phenanthroline was prepared and characterised by X-ray structure analysis and IR spectroscopy. Three complexes exhibit square-pyramidal coordination, whereas one exhibits octahedral coordination. The ligand 1,10-phenanthroline acts in a bidentate chelating mode with *N*,*N*-metal binding. The chloranilate dianion coordinates to the Cu^{II} atom in a terminal bidentate *ortho*-quinone-like mode, forming a 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 mode through a carboxy oxygen of a symmetry-related dianion leads to the formation of polymeric coordination ribbon. The crystal packing of penta-coordinated species, in addition to hydrogen bonding, involves less common stacking interactions of chelate rings with the 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] Of these compounds, complexes of transition metals and organic π-functional ligands have been intensively studied. It is well known that in the design of mono- and polynuclear (homo- and hetero-) complexes as new functional materials with desirable physical properties (mechanical, optical, electrical, or magnetic), an important role belongs to the oxalate $C_2O_4^{2-}$ 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 example of oxalate complexes as precursors in the synthesis of novel nanocrystalline mixed metallic oxides[11–13] has been widely exploited.

Thus, our recent (magneto)structural studies on oxalate-based metal complexes[14–17] have been extended to the reactions of the similar, but more stretched, chloranilate dianion (Scheme 1) and transition metals. Our research aims to prepare novel (multi)functional materials using quinoid systems.[18–20] The proper selection of mixed organic ligands to complex suitable metal ions should lead to desired architectures and properties. However, the large number of compounds obtained during these syntheses, among which a limited number reveal the desired properties, means that entirely controlled syntheses are yet to be reported.



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

The 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.

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

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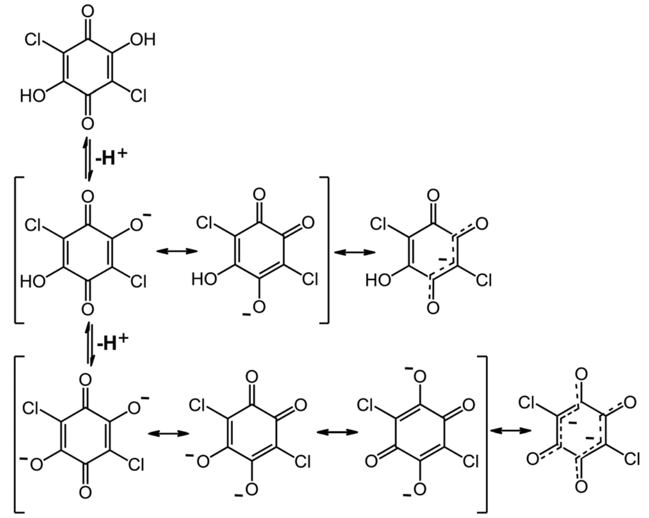
ligands 2,2′-bipyridine[18] and its congener, 1,10-phenanthroline (in the present work). It is of interest to prepare mixed complex species to resolve the impact of the binding mode of both ligands on metal coordination and crystal packing. In the series of Cu^{II} mixed complexes with chloranilic acid, coordinating in a terminal bidentate *ortho*-quinone-like mode, mononuclear species have been observed independently with the use of 2,2′-bipyridine[18] or 1,10-phenanthroline ligands. In the case of Cu^{II} complexes, an addition of bidentate chelating N-ligands generally favours the formation of mononuclear units[18] (as confirmed by the presented results in this study).

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 the crystal packing. A striking example is the recently described preparation, structure and magnetic properties of the stable 1,2,5[thiadiazolo][3,4-*f*][1,10-phenanthroline 1,1-dioxide] radical anion which combines the strong electron-withdrawing properties 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]

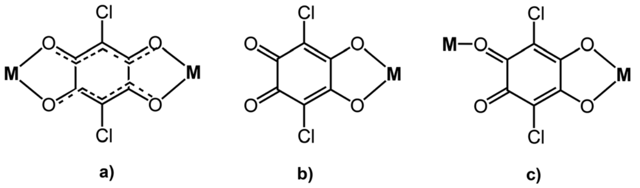
The selection of chloranilic acid and 1,10-phenanthroline for the synthesis of the complexes was motivated by the highly functionalised properties of both ligands. A variety of electrical and magnetic properties can be engineered by a simple combination of quinones, metals and other ancillary ligands.[4,22] The electronic properties of conjugated systems can be modified, thus allowing a wide variety of electrical and magnetic properties. Among the most interesting candidates for the 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 the 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 are especially promising for the synthesis of novel functional materials. They are strong proton donors and acceptors[25] which are capable of forming various kinds of hydrogen bonds. The acidity of the 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 pK_a values of 2.73 and 5.18, respectively[26]), but its dinitro analogue is a very strong acid comparable to sulfuric or perchloric acid (its pK_a values being −3.0 and −0.5, respectively[26]).

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 the 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 the polymeric species known,[35] there is an example of the structure comprising the chloranilate dianion and 1,10-phenanthroline ligands that we used to prepare the complexes presented in this work. The bidentate chloranilate dianion acting as a double bridging ligand generates zig-zag polymeric eight-coordinated Cd(II) chains connected into a 3D structure by stacking interactions between phen ligands arranged in an offset face-to-face fashion.

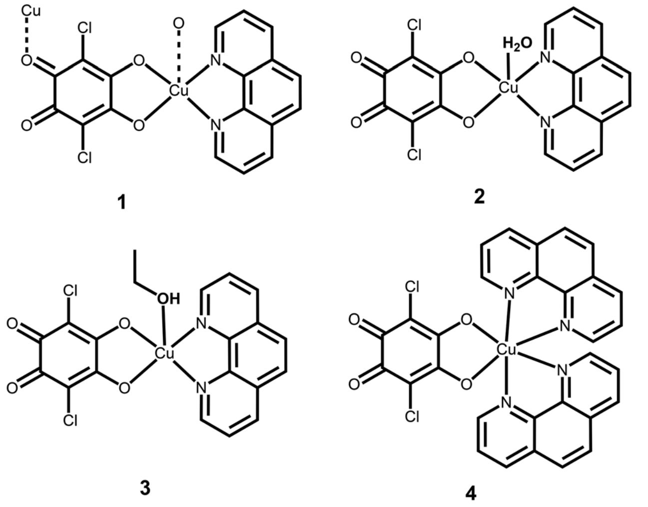


Scheme 2 Dissociation of chloranilic acid to the monoanion and dianion, with resonance structures shown in brackets.



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 bidentate + bridging monodentate mode observed for the first time in this study, which leads to the formation of polynuclear species.

The self-assembly of metal complexes with organic ligands, and sometimes solvents or guest molecules, based on combinations of intramolecular and intermolecular interactions reveals 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 4 Complexes described in this paper.

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 nitrogens juxtaposed, in contrast to 2,2′-bipyridine where a free rotation about the linking bond is possible. However, the 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 forms metal complexes. The introduction of hydrophobic and bulky ligands into complexes is verified to be an effective way to enhance their stability, whereas their bulkiness reduces 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] catalysis[43] and as components of supramolecular structures.[44] On the other hand, the ligand planarity allows 1,10-phenanthroline to act as an intercalating or groove-binding species with DNA and RNA,[45,46] and also as a 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 is abbreviated as CA) and 1,10-phenanthroline (abbreviated as phen) with copper(II) (Scheme 4). A novel, bidentate + bridging coordination mode of chloranilic acid is described (Scheme 3c), which has been observed for the first time.

Results and discussion

Molecular structures

The novel mixed-ligand copper(II) complexes were prepared: $[Cu(CA)(phen)]_n$, (**1**), $[Cu(CA)(phen)(H_2O)]\cdot H_2O$, (**2**), $[Cu(CA)(phen)(C_2H_5OH)]$, (**3**), all three in the square-pyramidal coordination, and $[Cu(CA)(phen)_2]\cdot CH_3OH$, (**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.

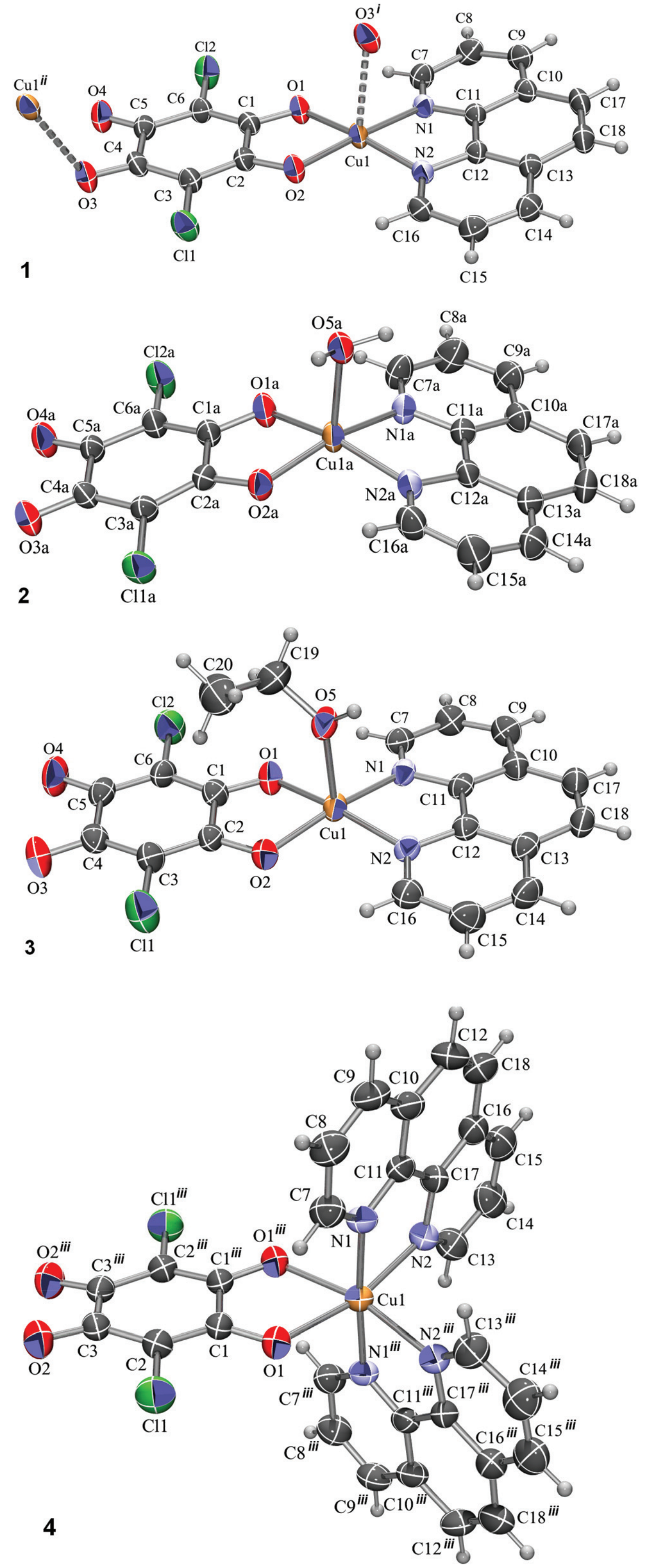


Fig. 1 Penta and hexa-coordinated complexes of: $[Cu(CA)(phen)]_n$, **1**, $[Cu(CA)(phen)(H_2O)]\cdot H_2O$, **2** (molecule a), $[Cu(CA)(phen)(C_2H_5OH)]$, **3**, and $[Cu(CA)(phen)_2]\cdot CH_3OH$, **4**. Displacement ellipsoids are drawn at the probability of 50% and hydrogen atoms are shown as spheres of arbitrary radii. Symmetry operators: (*i*) $1 - x, 1/2 + y, 1/2 - z$; (*ii*) $1 - x, -1/2 + y, 1/2 - z$; (*iii*) $1 - x, y, 1/2 - z$.

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	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	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	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	91.42(8)	N1–Cu1–O5	95.76(8)	99.22(8)	97.67(19)
N1–Cu1–O3^i	85.25(8)	N2–Cu1–O5	92.64(8)	90.80(8)	94.5(2)
	4				
Cu1–N1^{ii}	2.016(2)				
Cu1–N1	2.016(2)				
Cu1–N2	2.161(3)				
Cu1–N2^{ii}	2.161(3)				
Cu1–O1	2.161(2)				
Cu1–O1^{ii}	2.161(2)				
N1^{ii}–Cu1–N1	175.73(11)				
N1^{ii}–Cu1–N2	80.10(10)				
N1^{ii}–Cu1–N2^{ii}	97.05(10)				
N1^{ii}–Cu1–O1	92.21(10)				
N1^{ii}–Cu1–O1^{ii}	91.15(10)				
N1–Cu1–N2	97.05(10)				
N1–Cu1–N2^{ii}	80.10(10)				
N1–Cu1–O1	91.15(10)				
N1–Cu1–O1^{ii}	92.21(10)				
N2–Cu1–N2^{ii}	97.34(10)				
N2–Cu1–O1	93.88(9)				
N2–Cu1–O1^{ii}	166.52(9)				
N2^{ii}–Cu1–O1	166.52(9)				
N2^{ii}–Cu1–O1^{ii}	93.88(9)				
O1–Cu1–O1^{ii}	76.10(9)				

Their crystal structures and infrared spectroscopic characteristics are described.

The bite angles of the bidentate phen and chloranilate ligands are considerably less than 90° (Table 1), significantly contributing to the coordination polyhedra distortion. The compound $[\mathrm{Cu(CA)(phen)}]_n$ (**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*, 1/2 + *y*, 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[48]), but it is shorter than the sum of the van der Waals radii (2.92 Å). According to the Cambridge Structural Database,[49] the distribution of Cu–O bonds is bimodal, with the average values of 1.95(4) Å and 2.36(16) Å; the larger value corresponds to longer distances observed in the 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] The penta-coordination mode in Cu$^{\mathrm{II}}$ complexes reveals square-pyramidal and trigonal-bipyramidal coordinations. The square planar, four-coordination mode, typical of the d^9 configuration in Cu$^{\mathrm{II}}$ complexes, is of high kinetic stability in comparison with penta-coordination.[53] The phen ligand is slightly twisted out of the equatorial plane with the Cremer–Pople[54] puckering parameter Q = 0.176(3) Å.

In $[\mathrm{Cu(CA)(phen)(H_2O)}]\cdot\mathrm{H_2O}$ (**2**) and $[\mathrm{Cu(CA)(phen)(C_2H_5OH)}]$ (**3**), water and ethanol molecules are coordinated at the apical position of the square-pyramid (Fig. 1). The phen ligands in **2** are slightly twisted (with puckering amplitudes[54] of 0.159(3) and 0.086(3) Å for molecules **a** and **b**, respectively) and the angle between the mean planes of the chloranilate and phen ligands are 18.7° and 19.2°, respectively. However, **3** is more planar, with the mean planes of phen and chloranilate being inclined by only 1.0°; the puckering amplitude of phen is 0.209(7) Å. The copper atom is displaced by 0.129 Å above the least-squares plane of the phen and CA ligands.

In $[\mathrm{Cu(CA)(phen)_2}]\cdot\mathrm{CH_3OH}$ (**4**), two phen ligands are coordinated to the Cu$^{\mathrm{II}}$ in an octahedral arrangement together with the ligand CA (Fig. 1), revealing the C_2 molecular symmetry. The octahedron is significantly distorted due to the O–Cu–O and N–Cu–N bite angles, which are considerably smaller than 90° (Table 1).

The geometry of the chloranilate ligand (Table 2) is somewhere between a dianion and an *o*-quinone (Scheme 2), as

Table 2 Bond lengths in the chloranilate dianion (Å)

	1	**2a**	**2b**	**3**	**4**[a]
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–Cl1	1.743(3)	1.731(3)	1.730(3)	1.731(6)	1.744(4)
C6–Cl3	1.734(3)	1.725(3)	1.726(3)	1.735(6)	1.744(4)

[a] Equivalent bonds; due to the molecular symmetry C_2, the labelling is different.

found in similar mononuclear complexes with bpy as the ancillary ligand,[18] and it appears to be usual when a 2,5-dihydroxyquinolate 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 the uncoordinated bonds 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 the bidentate chloranilate anion for compounds **1–4** are given in Table 3.[55] The red and blue shifts of the observed position of ν(C=C) and ν(C–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 the chloranilate dianion to the copper(II) atoms in a bridging mode, leading to the formation of the polymeric ribbon. Other absorption bands of significant intensities 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 a maximum around 3420 cm^{-1} in the spectrum of compound **2** originates from the O–H stretching vibration [ν(OH)], and is in agreement with the presence of 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 [ν(OH)] of alcohol solvates involved in the intermolecular hydrogen bonds.[55]

Crystal packing

In the series studied, penta-coordinated complexes crystallized in noncentrosymmetric space groups, whereas the octahedral complex reveals C_2 molecular symmetry with Cu$^{\text{II}}$ located on a twofold rotation axis in the space group $C2/c$. The topology of their packing patterns is entirely different (Fig. 2–7). The two types of interactions occur in their crystal packing: hydrogen bonding occurs in **3** and **4**, whereas in **1**, only stacking interactions are encountered. However, the crystal packing of **2** reveals intensive interactions of both types (Tables 4 and 5). In **3**, both types of intramolecular interactions are presented, including hydrogen bonding between ethanol molecules and chloranilate, and phen⋯chloranilate stacking interactions (Tables 4 and 5). In complexes **2** and **3** with ligands exhibiting proton donor and acceptor functionalities, hydrogen bonding interactions affect their crystal packing (Table 5, Fig. 4–6). The crystal solvent molecules in **2** and **4** play a role in their crystal packing *via* the formation of hydrogen bonds (Table 5). Due to a lack of proton donor/acceptor functionalities in **1**, hydrogen bonding is not possible. However, the crystal packing of **1** is dominated by stacks of (a) Cu–O–chloranilate chelate rings with phen rings, (b) Cu–N–chelate–phen rings

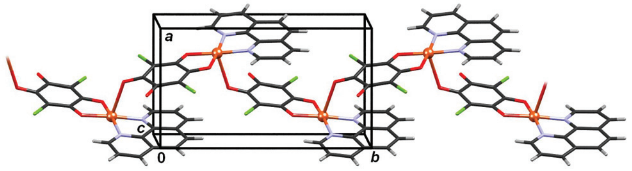


Fig. 2 A polymeric ribbon of **1** extending in the [010] direction.

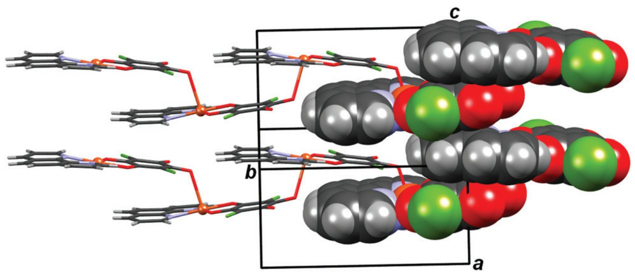


Fig. 3 π-Interactions between two contiguous coordination polymers of **1** reveal stacking of the 1,10-phenanthroline and chloranilate moieties. To emphasize the stacking, a pair of [Cu(CA)(phen)] units has been depicted as van der Waals spheres.

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

Compound	ν(C=C)	ν(C=O)	ν(C–O)	ν(C–C)	ν(C–Cl)	δ(CC=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	1648	1632, 1614	1374	999	845	668	574
4	1647	1635, 1614	1374	999	845	668	574

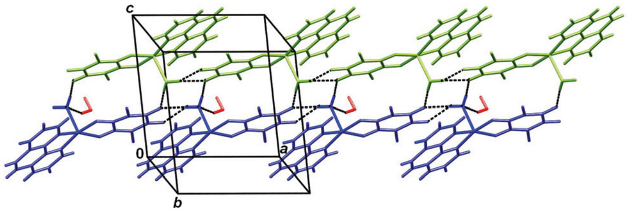


Fig. 4 Crystal packing of **2**, composed of hydrogen bonded chains of the two symmetry-independent molecules **a** (green) and **b** (blue).

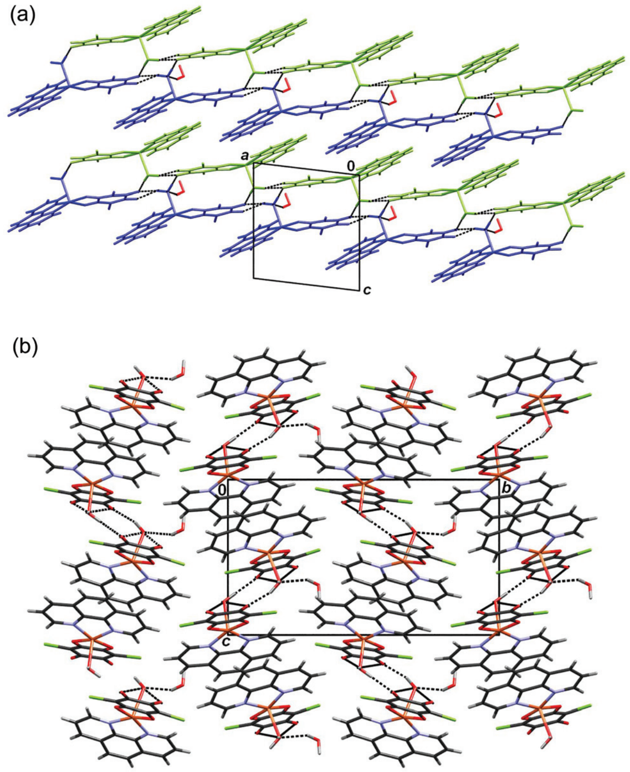


Fig. 5 (a) Stacking of 1,10-phenanthroline ligands between hydrogen bonded chains in **2** generating layers parallel to the (101) plane; (b) packing of the layers viewed in the [100] direction.

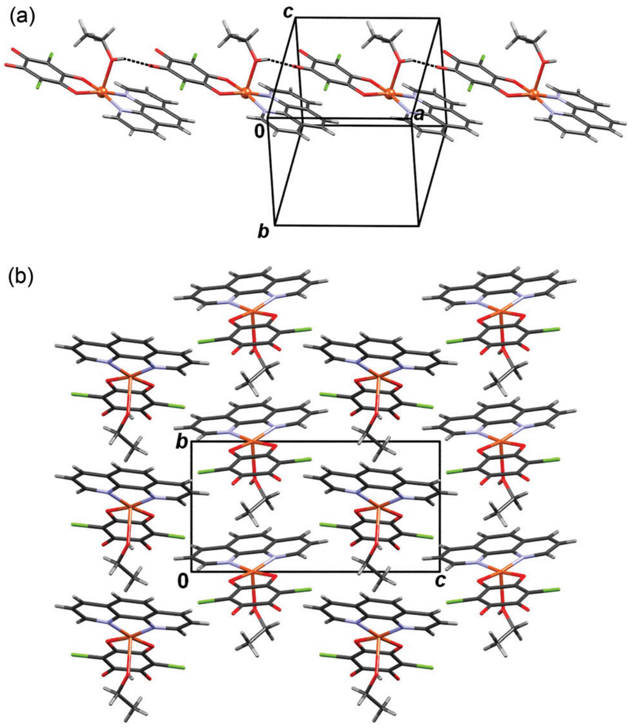


Fig. 6 (a) Hydrogen bonded chain of **3** parallel to [100]; (b) packing of these chains viewed in the [100] direction.

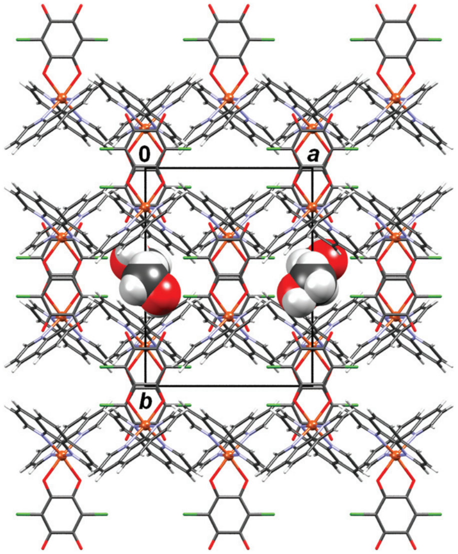


Fig. 7 Crystal packing of **4** viewed in the [001] direction with channels occupied by disordered MeOH molecules, presented by van der Waals spheres.

with phen rings (Fig. 8), and (c) chloranilate⋯phen rings (Table 4, Fig. 3 and 8). 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 as follows (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 the rings is observed in the crystal packing of **2** and **3**, whereas in **1** there is no offset. The geometrical parameters point 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]

Compound **1** reveals a polymeric coordination chain of [Cu(CA)(phen)] units linked by the long Cu–O3^i [symmetry

Table 4 Geometric parameters of the π-interactions

π⋯π	Cg[a]⋯Cg/Å	α[b]	β[c]	Cg⋯plane(Cg2)/Å	Offset[d]/Å	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 the planes of two interacting rings. [c] β = angle between the Cg⋯Cg line and the normal to the plane of the first interacting ring. [d] Offset can be calculated only for the strictly parallel rings (α = 0.00°). For slightly inclined rings ($\alpha \leq 5°$) an approximate value is given.

Table 5 Geometric parameters of hydrogen bonds

	D–H/Å	H⋯A/Å	D⋯A/Å	D–H⋯A/°	Symm. op. on A
2					
O5a–H5a⋯O4b	0.92(3)	1.86(3)	2.777(3)	176(3)	$1 - x, 1/2 + y, 1 - z$
O5a–H5b⋯O3a	0.93(2)	2.29(4)	3.018(3)	135(4)	$1 + x, y, z$
O5a–H5b⋯O4a	0.93(2)	2.04(4)	2.852(3)	135(4)	$1 + x, y, z$
O5b–H5c⋯O3a	0.83(4)	2.06(4)	2.841(5)	158(5)	x, y, z
O5b–H5d⋯O3b	0.93(3)	1.86(4)	2.755(3)	161(3)	$1 - x, -1/2 + y, 1 - z$
O5b–H5d⋯O4b	0.94(2)	2.19(5)	2.983(3)	143(6)	$1 + x, y, z$
O6–H6b⋯O5b	0.97(9)	2.06(9)	2.958(5)	152(6)	x, y, z
3					
O5–H5⋯O4	0.82(4)	2.06(5)	2.844(7)	161(6)	$1 + x, y, z$
O5–H5⋯O3	0.82(4)	2.46(5)	2.939(7)	118(6)	$1 + x, y, z$
4					
O3–H3⋯O2	0.82	2.31	2.764(8)	115	x, y, z
C7–H7⋯O3	0.93	2.77	3.247(9)	121	$3/2 - x, -1/2 + y, 1/2 - z$
C9–H9⋯O2	0.93	2.61	3.473(7)	154	$x, 1 - y, -1/2 + z$
C9–H9⋯Cl1	0.93	2.91	3.643(8)	136	$x, 1 - y, -1/2 + z$
C13–H13⋯Cl1	0.93	2.92	3.662(7)	138	$3/2 - x, -1/2 + y, 1/2 - z$

operator (*i*) $1 - x, 1/2 + y, 1/2 - z$] bond extending in the [010] direction (Fig. 2). Lacking proton donor sites, these chains are stacked through interactions of various π-systems, forming layers parallel to the (110) plane (Fig. 3, Table 4). There are only dispersion interactions between these layers.

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 bonds, forming ladder-like double chains (**a** and **b** molecules) extending in the [100] direction (Fig. 4, Table 5). The crystal water molecule acts as a single proton donor in hydrogen bonds as a pendant to molecule **b** (Fig. 4). In the crystal packing of **2**, extensive hydrogen bonding, together with various combinations of π-interactions involving chelate, aromatic (phen), and quinoid (chloranilate) rings between chains, connects them into layers parallel to the (101) plane (Fig. 5). However, these layers are connected only by dispersion interactions.

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

Compound **4** crystallizes as a methanol solvate. The MeOH molecule is disordered, with its methyl group lying on the twofold rotation 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 O2 (chloranilate) of the same asymmetric unit (Table 5). Molecules of the complex are linked by C–H⋯O and C–H⋯Cl hydrogen bonds (Table 5). The

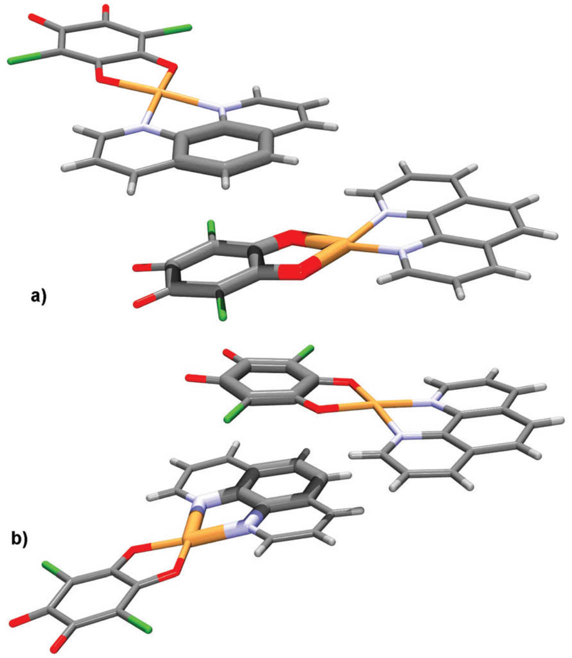


Fig. 8 π-Interactions involving chelate rings in the crystal packing of **1**: (a) interaction of the Cu–O–chelate ring with a phen ligand and (b) interaction of the Cu–N–chelate ring and chloranilate ligand.

porous crystal packing reveals channels running parallel to [001] that are filled by disordered methanol molecules (Fig. 7).

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 the asymmetric unit of **2**, the 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 the π-systems of the ligands (Table 4). In contrast, in the series of Cu^{II} complexes comprising chloranilate and bpy ligands, chelate⋯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 azobenzenes;[65–67] 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]

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 inhomogeneous due to the presence of free chloranilic acid; however a few crystals could be separated to measure the IR spectrum).

Preparation

Preparation of $[Cu(CA)(phen)]_n$ (1). After mixing a methanol solution (4 mL) of $CuCl_2·2H_2O$ (17.1 mg; 0.1 mmol) with a methanol solution (4 mL) of 1,10-phenanthroline (19.9 mg; 0.1 mmol), the 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 $[Cu(CA)(phen)(H_2O)]·H_2O$ (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 $CuCl_2·2H_2O$ (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 $C_{36}H_{22}Cl_4Cu_2N_4O_{11}$ (M_r = 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 $[Cu(CA)(phen)(C_2H_5OH)]$ (3). Aqueous solutions of $CuCl_2·2H_2O$ (17.7 mg; 0.1 mmol; 3 mL) and 1,10-phenanthroline (19.9 g; 0.1 mmol; 3 mL) were mixed by heating. The resulting solution was put into a test tube. Next, 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 $C_{18}H_8Cl_2CuN_2O_4$ (M_r = 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 $[Cu(CA)(phen)]·CH_3OH$ (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,

Table 6 Crystallographic, data collection and structure refinement details

Compound	1	2	3	4
Empirical formula	$C_{18}H_8Cl_2CuN_2O_4$	$C_{36}H_{22}Cl_4Cu_2N_4O_{11}$	$C_{20}H_{14}Cl_2CuN_2O_5$	$C_{31}H_{30}Cl_2CuN_4O_5$
Formula wt/g mol^{-1}	450.72	955.49	496.79	662.98
Crystal dimensions/mm	0.25 × 0.12 × 0.07	0.20 × 0.18 × 0.02	0.22 × 0.10 × 0.05	0.16 × 0.10 × 0.06
Space group	$P2_12_12_1$	$P2_1$	$P2_1$	$C2/c$
a/Å	7.44480(10)	9.53230(10)	9.00760(10)	12.3532(6)
b/Å	13.1466(2)	18.0066(2)	7.42350(10)	15.0096(7)
c/Å	16.0004(3)	10.39350(10)	14.1624(2)	16.3027(8)
α/°	90	90	90	90
β/°	90	96.8220(10)	90.8730(10)	111.011(6)
γ/°	90	90	90	90
Z	4	2	2	4
V/Å^3	1566.02(4)	1771.35(3)	946.90(2)	2821.8(2)
D_{calc}/g cm^{-3}	1.912	1.791	1.742	1.561
μ/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
T/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 h, k, l	$-9 < h < 6$; $-9 < k < 16$; $-19 < l < 17$	$-11 < h < 7$; $-22 < k < 19$; $-13 < l < 12$	$-6 < h < 11$; $-9 < k < 8$; $-17 < l < 17$	$-15 < h < 15$; $-16 < k < 18$; $-20 < l < 16$
Reflections collected	4842	8683	4733	6044
Independent reflections	2853	5400	2775	2815
Observed reflections ($I \geq 2\sigma$)	2771	5287	2724	2417
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
R_{int}	0.0211	0.0215	0.0212	0.0448
R (F)	0.0303	0.0273	0.0724	0.0467
R_w (F^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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.403; −0.392	0.425; −0.453	1.219; −1.177	0.526; −0.637

the thin crystals contain phenanthroline and H_2CA molecules, but the crystals were not of the quality needed for X-ray analysis). The resulting violet solution was layered with a methanol solution (8 mL) of $CuCl_2{\cdot}2H_2O$ (17.1 mg; 0.1 mmol) in 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) instrument 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. The CrysAlis PRO[71] program package was used for data reduction. The structures were solved using SHELXS97[72] 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: the geometry of water molecules was constrained to d(O–H) = 0.95(2) Å; d(H⋯H) = 1.50(4) Å, and the hydroxyl group to d(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, the geometry of the methanol molecule is not realistic due to the disorder.

Molecular geometry calculations were performed by PLATON,[73] and the 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.

CCDC 973343–973346 contain the supplementary crystallographic data for this paper.

Conclusions

In mixed ligand complexes of Cu^{II} comprising chloranilate and phen ligands, square-pyramidal coordination is predominant. In a single case is an octahedral coordination found. The *N*,*N*-ligand binding of phen has a significant impact on the 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. The 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 (chloranilate and aromatic phen rings) in a 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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