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Two centrosymmetric dinuclear phenanthroline–copper(II) complexes with 3,5-dichloro-2-hydroxybenzoic acid and 5-chloro-2-hydroxybenzoic acid

Ján Moncol,[a]* Klaudia Jomová[b] and Mária Porubská[b]

[a]Department of Inorganic Chemistry, Faculty of Chemical and Food Technology, Slovak Technical University, SK-812 37 Bratislava, Slovakia, and [b]Faculty of Natural Sciences, Constantine the Philosopher University in Nitra, SK-949 74 Nitra, Slovakia
Correspondence e-mail: jan.moncol@stuba.sk

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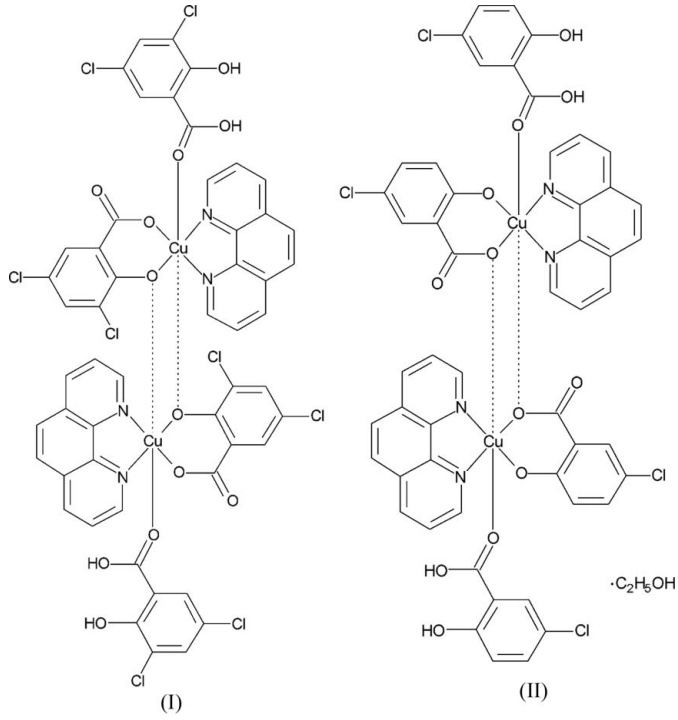
The title compounds, bis(μ-3,5-dichloro-2-oxidobenzoato)-$\kappa^3O^1,O^2:O^2;\kappa^3O^2:O^1,O^2$-bis[(3,5-dichloro-2-hydroxybenzoic acid-κO^1)(1,10-phenanthroline-κ^2N,N')copper(II)], $[Cu_2(C_7H_2Cl_2O_3)_2(C_7H_4Cl_2O_3)_2(C_{12}H_8N_2)_2]$, (I), and bis($\mu$-5-chloro-2-oxidobenzoato)-$\kappa^3O^1,O^2:O^1;\kappa^3O^1:O^1,O^2$-bis[(5-chloro-2-hydroxybenzoic acid-κO^1)(1,10-phenanthroline-κ^2N,N')copper(II)] ethanol monosolvate, $[Cu_2(C_7H_3ClO_3)_2(C_7H_5ClO_3)_2(C_{12}H_8N_2)_2]\cdot C_2H_6O$, (II), contain centrosymmetric dinuclear complex molecules in which Cu^{2+} cations are surrounded by a chelating 1,10-phenanthroline ligand, a chelating 3,5-dichloro-2-oxidobenzoate or 5-chloro-2-oxidobenzoate anionic ligand and a monodentate 3,5-dichloro-2-hydroxybenzoic acid or 5-chloro-2-hydroxybenzoic acid ligand. The chelating benzoate ligand also bridges to the other Cu^{2+} ion in the molecule, but the O atom involved in the bridge is different in the two complexes, being the phenolate O atom in (I) and a carboxylate O atom in (II). The bridge completes a 4+1+1 axially elongated tetragonal–bipyramidal arrangement about each Cu^{2+} cation. The complex molecules of both compounds are linked into one-dimensional supramolecular chains through O—H$\cdots$O hydrogen bonds.

Comment

Many copper complexes with a variety of organic chelating ligands have been shown to possess biological activities, including anti-inflammatory and anticonvulsant properties (Lemoine *et al.*, 2002), cytotoxicity and antiviral activity (Ranford *et al.*, 1993). Several copper(II) complexes acting as proteasome inhibitors capable of inducing programmed cell death (apoptosis) have been prepared and characterized. In these complexes, the metal ion is coordinated to heteroatomic neutral ligands such as the 1,10-phenanthroline ligand (Marzano *et al.*, 2009). It has been reported that the copper complex with 1,10-phenanthroline is able to induce the formation of free radicals which in turn degrade DNA under *in vitro* conditions. The mechanism of action of this complex is derived from the potential intercalation of planar phenanthroline into DNA and the *in situ* generation of free radicals, predominantly hydroxy radicals mediated by the presence of copper (Sigman, 1986; Sigman *et al.*, 1993). In these aspects, copper complexes with the chelating 1,10-phenanthroline ligand can be used as anticancer agents (Tardito & Marchio, 2009; Tisato *et al.*, 2010).



(I) (II)

Salicylic acid (2-hydroxybenzoic acid; $salH_2$) and its substituted derivatives can be coordinated as neutral molecular ligands or as anionic ligands with deprotonated carboxylic acid ($salH^-$) or deprotonated carboxylic acid and hydroxy groups (sal^{2-}). These ligands may coordinate in a chelating and/or bridging fashion. In view of these properties, in this preliminary contribution, we directed our attention to the preparation and structural characterization of potentially bioactive copper(II)–1,10-phenanthroline complexes with anions of two derivatives of salicylic acid.

The structure of bis(μ-3,5-dichloro-2-oxidobenzoato)bis-[(3,5-dichloro-2-hydroxybenzoic acid)(1,10-phenanthroline)-copper(II)], (I) (Fig. 1), exhibits a centrosymmetric dinuclear molecular structure. Two Cu atoms are organized in a dimeric unit *via* the bridging O atoms of the phenolate groups of 3,5-dichloro-2-oxidobenzoate anions [O3 and O3^i; symmetry code: (i) $-x+1, -y+1, -z+1$]. Each Cu atom in the dimeric unit is hexacoordinated (Table 1) in an axially stretched tetragonal–bipyramidal geometry by the phenolate and carboxylate O atoms, O3 and O1, respectively, of the chelating bridging 3,5-dichloro-2-oxidobenzoate anion and the two N atoms of the 1,10-phenanthroline ligand, which complete the equatorial plane, while the axial positions are occupied by the

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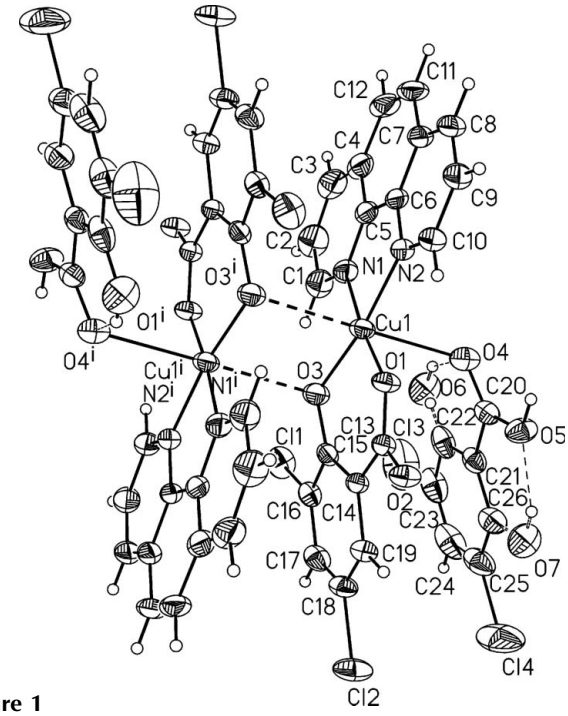

Figure 1
A perspective view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Both positions of the disordered hydroxyphenyl group (O6/O7) are shown. The thin dashed lines indicate intramolecular hydrogen bonds. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

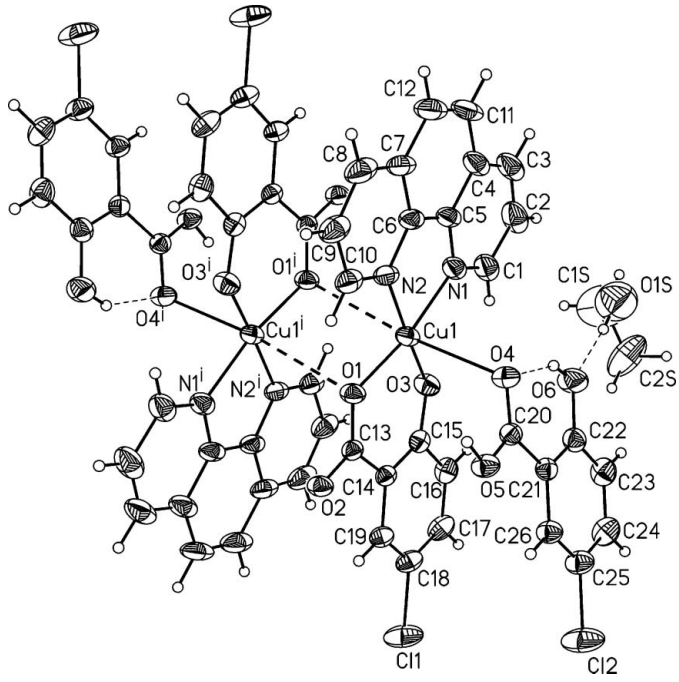

Figure 2
A perspective view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The thin dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

phenolate O atom from the second symmetry-related bridging 3,5-dichloro-2-oxidobenzoate anion and the carboxylic acid O atom, O4, of the monodentate 3,5-dichloro-2-hydroxybenzoic acid ligand. This complex represents the first example of a dinuclear complex of sal^{2-} in which the phenolate O atom is both bridging and chelating. Interestingly, a three-atom carboxylate bridging ligand (Cu—O—C—O—Cu) in a dimeric copper(II) sal^{2-} complex was reported recently by Weng *et al.* (2007).

The crystal structure of bis(μ-5-chloro-2-oxidobenzoato)-bis[(5-chloro-2-hydroxybenzoic acid)(1,10-phenanthroline)-copper(II)] ethanol monosolvate, (II) (Fig. 2), consists of centrosymmetric dinuclear complex molecules and disordered ethanol solvent molecules (see *Experimental*). The structure of the dinuclear complex and the coordination geometry (Table 3) of the Cu^{2+} ions in (II) are very similar to those in (I), with the exception that the bridges between the Cu^{2+} ions involve the carboxylate O atom, O1, of the chelating bridging 5-chloro-2-oxidobenzoate anion, instead of the phenolate O atom. The axial Cu1—O1^{i} [symmetry code: (i) $-x+1, -y+1, -z+1$] bond of 2.984 (2) Å involving this bridging O atom is about 0.27 Å longer than the Cu1—O3^{i} bond in (I), although it is in the range found for copper(II) complexes with tetragonal–bipyramidal coordination around the Cu^{2+} ion (Melnik, Kabesova, Koman *et al.*, 1998; Melnik, Kabesova, Macaskova *et al.*, 1998) possessing Jahn–Teller distortions (Gazo *et al.*, 1976).

The molecular structures of (I) and (II) revealed the existence of two alternative coordination modes of sal^{2-} anions through bridging phenolate or carboxylate O atoms. The appearance of different binding modes of the bridging sal^{2-} ligands could be attributed to the almost identical energy of both structural configurations. More insight into this phenomenon might be obtained from theoretical calculations. The Cu1$\cdots$Cu1^{i} distance of 3.3456 (5) Å for (I), which has bridging phenolate O atoms, is close to the range of 3.15–3.31 Å found in dinuclear copper(II) sal^{2-} complexes with bridging phenolate O atoms (Lemoine *et al.*, 1999, 2000, 2002; Fan *et al.*, 2005; Hu *et al.*, 2007; Nie *et al.*, 2010; Palanisami *et al.*, 2006; Geraghty *et al.*, 1999; Wang & Okabe, 2004). On the other hand, dinuclear complex (II) has a longer Cu1$\cdots$Cu1^{i} distance of 3.5709 (5) Å. We note that the Cu$\cdots$Cu distance in the dimeric complex with a three-atom bridging sal^{2-} ligand has been reported to be 4.93 Å (Wen *et al.*, 2007). The Cu^{2+} ions in both (I) and (II) are coordinated by six donor atoms and they represent the first two examples of copper(II) sal^{2-} complexes with coordinated salicylic acid as a ligand; all other known dimeric copper(II) sal^{2-} complexes are coordinated by five atoms (two pyridine N atoms of 1,10-phenanthroline or 2,2′-bipyridine and three O atoms of phenolate and carboxylate groups of sal^{2-} bridging anionic ligands or their derivatives). The Cu atoms in monomeric copper(II) sal^{2-} complexes have a square-planar coordination environment formed by two pyridine N atoms and two O atoms of sal^{2-} anions (Zhang *et al.*, 2007*a*,*b*) or a square-pyramidal coordination environment formed by the same atoms in a square plane with additional O or N atoms in the apical position from another ligand such as water (Gao *et al.*, 2009; Zhang *et al.*, 2008; Yu *et al.*, 2009) or pyridine (Wen *et al.*, 2007), respec-

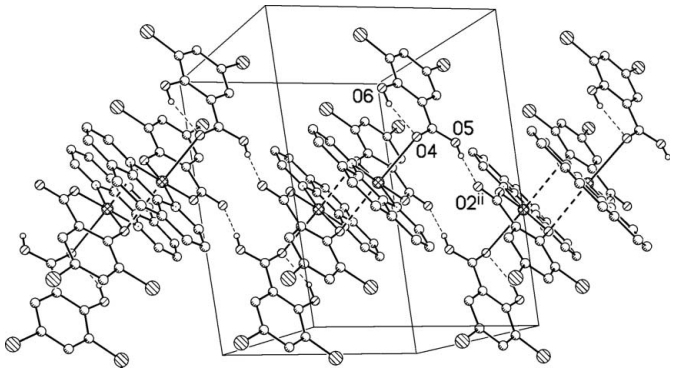

Figure 3
The crystal structure of (I). H atoms of the aromatic rings have been omitted for clarity. The thin dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x+2, -y+1, -z+1$.]

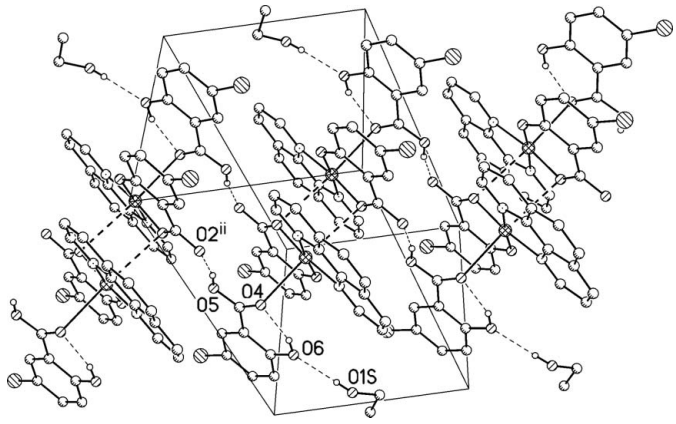

Figure 4
The crystal structure of (II). H atoms of the aromatic rings and ethyl groups have been omitted for clarity. The thin dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x+2, -y+1, -z+1$.]

tively. In the known complexes, the distances between the Cu atom and the O atom from axially coordinated bridging sal^{2-} ligands in dinuclear complexes are in the range of 2.28–2.65 Å, but the Cu—L_{ax} (ax is axial) bond distances in monomeric complexes are in a narrower range (2.26–2.35 Å).

The aromatic rings of the benzoate, benzoic acid and 1,10-phenanthroline ligands of both complexes are stacked (Figs. 1 and 2) and π–π stacking interactions (Janiak, 2000) are observed between the benzene ring of the sal^{2-} anion and the benzene ring of the salicylic acid ligand. The distances between the planes of the two benzene rings are in the range 3.34–3.68 Å for (I) and 3.27–3.84 Å for (II) (Table 5). Further π–π stacking interactions (Janiak, 2000) are observed between the benzene ring of the sal^{2-} anion and adjacent aromatic rings of 1,10-phenanthroline ligands at $(-x+1, -y+1, -z+1)$, with the separation between the planes of the aromatic rings in the range 3.16–3.99 Å for (I) and 3.24–3.70 Å for (II) (Table 5).

The centroid–centroid distances in (I) are 3.732 (2) Å between the benzene ring (C14–C19) of the 3,5-dichloro-2-oxidobenzoate anion and the benzene ring (C21–C26) of the 3,5-dichloro-2-hydroxybenzoic acid molecule, and 3.837 (2) Å between the C14–C19 benzene ring and the benzene ring (C4–C7/C11/C12) of the 1,10-phenanthroline ligand in the molecule at $(-x+1, -y+1, -z+1)$. The centroid–centroid distances in (II) are 3.8030 (13) Å between the benzene ring (C14–C19) of the 5-chloro-2-oxidobenzoate anion and the benzene ring (C21–C26) of the 5-chloro-2-hydroxybenzoic acid molecule, and 3.5754 (13) Å between the C14–C19 benzene ring and the N2/C6–C10 pyridine ring of the 1,10-phenanthroline ligand in the molecule at $(-x+1, -y+1, -z+1)$.

The crystal packing in (I) and (II) is shown in Figs. 3 and 4, respectively. The complex molecules of both compounds are connected into one-dimensional supramolecular chains through O5—H5O···O2^{ii} hydrogen bonds [Tables 2 and 4; symmetry code: (ii) $-x+2, -y+1, -z+1$] between the carboxylic acid H atom of a monodentate 3,5-dichloro-2-hydroxybenzoic acid ligand or a 5-chloro-2-hydroxybenzoic acid ligand and the uncoordinated O atom of the carboxylate group of a chelating 3,5-dichloro-2-oxidobenzoate or a 5-chloro-2-oxidobenzoate anion of a neighbouring molecule. The disordered uncoordinated ethanol solvent molecules of (II) are connected through an O1S—H1S···O6 hydrogen bond to the hydroxy O atom of a monodentate 5-chloro-2-hydroxybenzoic acid ligand. The crystal structure of (II) is observed also to have a short Cl2···Cl2^{iii} contact (Desiraju, 1995) [symmetry code: (iii) $-x+3, -y+1, -z$], with an interatomic distance of 3.2569 (14) Å.

In this contribution, we report the crystal structures of two copper(II)–1,10-phenanthroline complexes with derivatives of salicylic acid. The structural study revealed dinuclear complexes with hexacoordination around the Cu atom. Further work on the biological activity of the prepared complexes is in progress.

Experimental

The title copper complexes were prepared in a similar manner to methods described previously by Ranford *et al.* (1993). To the royal-blue solution formed from copper(II) acetate hydrate (0.200 g, 1 mmol) and 1,10-phenanthroline (0.182 g, 1.00 mmol) in ethanol (40 ml) was added 3,5-dichloro-2-hydroxybenzoic acid (0.207 g, 1 mmol) for (I) or 5-chloro-2-hydroxybenzoic acid (0.173 g, 1 mmol) for (II). The resulting mixture was stirred for 4 d and the green products were filtered off and washed with ethanol. The green filtrates were left to stand at room temperature for about two weeks giving crystals suitable for X-ray analysis. The compositions of the main product and the corresponding crystals obtained from the green filtrates were checked with IR measurements and were found to be identical.

Compound (I)

Crystal data

$[Cu_2(C_7H_2Cl_2O_3)_2(C_7H_4Cl_2O_3)_2(C_{12}H_8N_2)_2]$
M_r = 1311.48
Triclinic, $P\overline{1}$
a = 9.2295 (2) Å
b = 11.6047 (3) Å
c = 12.9863 (3) Å
α = 102.423 (2)°
β = 99.045 (2)°
γ = 106.753 (2)°
V = 1264.44 (5) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.33 mm^{-1}
T = 293 K
0.43 × 0.14 × 0.05 mm

Table 1
Selected bond lengths (Å) for (I).

Cu1—O3	1.881 (2)	Cu1—N1	2.011 (3)
Cu1—O1	1.906 (2)	Cu1—O4	2.585 (3)
Cu1—N2	1.990 (3)	Cu1—O3^{i}	2.716 (3)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5O···O2^{ii}	0.82	1.69	2.489 (3)	166
O6—H6O···O4	0.82	1.85	2.577 (5)	147
O7—H7O···O5	0.82	1.73	2.460 (14)	147

Symmetry code: (ii) $-x+2, -y+1, -z+1$.

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: analytical (*CrysAlis RED*; Agilent, 2011)
T_{min} = 0.598, T_{max} = 0.936
31426 measured reflections
5150 independent reflections
3886 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.160
S = 1.08
5150 reflections
363 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.85 e Å^{-3}

Compound (II)

Crystal data

$[Cu_2(C_7H_3ClO_3)_2(C_7H_5ClO_3)_2(C_{12}H_8N_2)_2]\cdot C_2H_6O$
M_r = 1219.78
Triclinic, $P\overline{1}$
a = 7.9153 (2) Å
b = 11.1877 (3) Å
c = 15.0623 (3) Å
α = 72.456 (2)°
β = 77.056 (2)°
γ = 83.897 (2)°
V = 1238.39 (5) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.15 mm^{-1}
T = 293 K
0.35 × 0.24 × 0.06 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: analytical (*CrysAlis RED*; Agilent, 2011)
T_{min} = 0.689, T_{max} = 0.934
20410 measured reflections
5017 independent reflections
4055 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.096
S = 1.06
5017 reflections
363 parameters
16 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

The 3,5-dichloro-2-hydroxybenzoic acid ligand of (I) has orientational disorder of the hydroxy group (O6/O7) and the site-occupation factors of the disordered parts are 0.807 (8) and 0.193 (8), respectively. The C—O distances involving these disordered hydroxy groups were restrained to 1.350 (1) Å, while the displacement parameters of the atoms at each end of these bonds were restrained to be similar (SIMU and DELU instructions in *SHELXL97*; Sheldrick, 2008).

The ethanol solvent molecule of (II) is disordered around an inversion centre. Distance restraints of 1.43 (1), 1.54 (1) and 2.38 (2) Å were applied to the O1*S*—C1*S*, C1*S*—C2*S* and O1*S*···C2*S* distances, respectively, while the displacement parameters of the solvent atoms were restrained to be similar (SIMU and DELU commands in *SHELXL97*).

The aromatic and methylene H atoms were positioned with C—H = 0.93 and 0.97 Å, respectively, and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C). The methyl H atoms were positioned with C—H = 0.98 Å and constrained to ride on their parent atoms with U_{iso}(H) = 1.5U_{eq}(C). The hydroxy/carboxylic acid H atoms were positioned with O—H = 0.82 Å and constrained to ride on their parent atoms with U_{iso}(H) = 1.5U_{eq}(C) using the AFIX 147 instruction for the nondisordered O—H group and AFIX 83 for the disordered O—H groups.

For both compounds, data collection: *CrysAlis CCD* (Agilent, 2011); cell refinement: *CrysAlis RED* (Agilent, 2011); data reduction: *CrysAlis RED*. Program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999) for (I); *SHELXS97* (Sheldrick, 2008) for (II). For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Table 3
Selected bond lengths (Å) for (II).

Cu1—O3	1.880 (1)	Cu1—N2	2.005 (2)
Cu1—O1	1.904 (1)	Cu1—O4	2.582 (2)
Cu1—N1	2.001 (2)	Cu1—O1^{i}	2.984 (2)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5O···O2^{ii}	0.82	1.67	2.472 (2)	165
O6—H6O···O4	0.82	1.83	2.560 (2)	147
O1*S*—H1*S*···O6	0.82	2.03	2.811 (7)	159

Symmetry code: (ii) $-x+2, -y+1, -z+1$.

Table 5
Geometrical parameters (Å, °) for π–π stacking interactions.

Complex	*Cg*–*Cg*^{a}	<(plane1–plane2)^{b}
(I)^{c}	3.73	7.6
(I)^{d}	3.84	16.9
(II)^{e}	3.80	11.7
(II)^{f}	3.58	9.2

Notes: (*a*) centroid–centroid distance; (*b*) the angle between the planes of the aromatic rings; (*c*) 3,5-dichloro-2-oxidobenzoate–3,5-dichloro-2-hydroxybenzoic acid; (*d*) 3,5-dichloro-2-oxidobenzoate–1,10-phenanthroline (*Cg* is the centroid of the phenanthroline benzene ring); (*e*) 5-chloro-2-oxidobenzoate–5-chloro-2-hydroxybenzoic acid; (*f*) 5-chloro-2-oxidobenzoate–1,10-phenanthroline (*Cg* is the centroid of a phenanthroline pyridine ring).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3164). Services for accessing these data are described at the back of the journal.

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