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# Zinc(II) and cadmium(II) chloride complexes with 4,4′-bi-1,2,4-triazole

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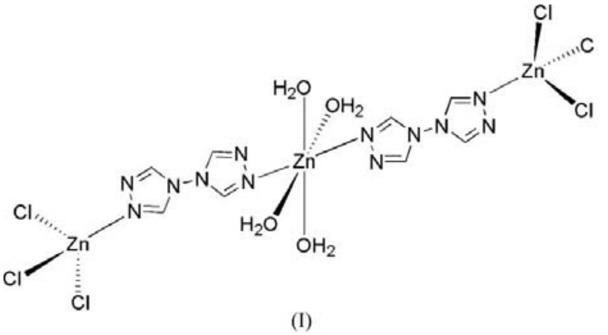
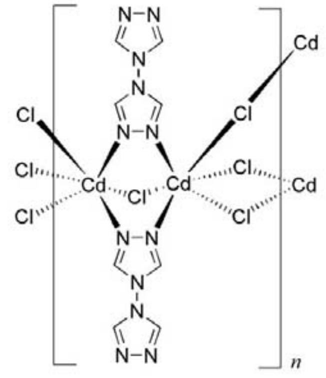
New coordination compounds with the 4,4′-bi-1,2,4-triazole ligand (btr), namely tetraaqua-2$\kappa^4O$-di-$\mu_2$-4,4′-bi-1,2,4-triazole-1:2$\kappa^2N^1$:$N^{1'}$;2:3$\kappa^2N^1$:$N^{1'}$-hexachlorido-1$\kappa^3Cl$,3$\kappa^3Cl$-trizinc(II), $[Zn_3Cl_6(C_4H_4N_6)_2(H_2O)_4]$, (I), and poly[cadmium(II)-$\mu_2$-4,4′-bi-1,2,4-triazole-$\kappa^2N^1$:$N^2$-di-$\mu_2$-chlorido], $[CdCl_2(C_4H_4N_6)]_n$, (II), reveal an unprecedented molecular zwitterionic structure for (I) and a polymeric two-dimensional layer structure for (II). Differences between these products, which involve the formation of either charge-separated chlorometallate/aquametal fragments or complementary organic and inorganic bridges, are attributable to the hardness–softness characters of the metal cations. In (I), two $N^1$,$N^{1'}$-bidentate btr molecules connect one $[Zn(H_2O)_4]^{2+}$ cation and two $[ZnCl_3]^-$ anions into a linear trizinc motif (the Zn atom of the cation occupies a centre of inversion in an $N_2O_4$ coordination octahedron, whereas the Zn atom of the anion possesses a distorted tetrahedral $Cl_3N$ environment). In (II), the distorted vertex-sharing $CdCl_4N_2$ octahedra are linked into binuclear $[Cd_2(\mu_2\text{-}Cl)(\mu_2\text{-}btr)_2]^{3+}$ fragments by unprecedented $N^1$:$N^2$-bidentate btr double bridges and bridging chloride ligands, while the additional chloride anions are also bridging, providing further propagation of the fragments into a two-dimensional network [Cd—Cl = 2.5869 (2)–2.6248 (7) Å].

## Comment

The co-operative assembly of small inorganic bridging anions (*e.g.* halogenides), short organic *N*-donor bridges (*e.g.* 1,2,4-triazole derivatives, trz) and transition metal cations provides many possibilities for the development of organic–inorganic frameworks. In a series of $Cd^{II}$ and $Zn^{II}$ 1,2,4-triazolates, the combined role of the anionic components is to connect the metal clusters and to participate in the framework connectivity (Ouellette *et al.*, 2007), while utilization of halogenide anions in $ZnF_2$-trz (Su *et al.*, 2004) and $CdCl_2$-trz (Yi *et al.*, 2004) leads to hollow tubular architectures and materials with luminescent properties. The use of the bitopic ligand 4,4′-bi-1,2,4-triazole (btr) instead of simple monofunctional triazole ligands involves the rational propagation of the characteristic nodal units into the lattice by means of the doubled triazole functionalities. In particular, such a combination of bitopic triazole and chloride bridges contributes to the formation of eight-connected coordination frameworks involving linear tricopper(II) secondary building blocks (Lysenko *et al.*, 2007). The combined behaviour of the btr molecule and $Cl^-$, as a co-ligand pair, is still unexplored. We wished to correlate this behaviour with the hardness–softness character of the metal cation. To this end, we have examined $Zn^{II}$/$Cd^{II}$–btr–$Cl^-$ systems and we report here the structures of two new complexes, $[Zn(H_2O)_4(\mu_2\text{-}btr)_2(ZnCl_3)_2]$, (I), and $[Cd(\mu_2\text{-}Cl)_2(\mu_2\text{-}btr)]_n$, (II).



(I)



(II)

The molecular trinuclear coordination compound, (I) (Fig. 1), is realized by consecutive interconnection of the Zn ions by two $N^1$,$N^{1'}$-bidentate btr bridges [Zn2—N4 = 2.0545 (18) Å and Zn1—N1 = 2.0930 (17) Å], and involves a cationic part (Zn1) and two outer anionic centres (Zn2). The central Zn1 atom of the cationic fragment lies on an inversion centre and possesses an octahedral $N_2O_4$ environment involving two N atoms from btr molecules in *trans* positions and four aqua ligands in the basal plane [Zn1—O = 2.136 (2) and 2.1091 (17) Å], as has been observed for zwitterionic Zn–pyridine complexes, *e.g.* $Zn(H_2O)_4$(pyridine-3-sulfonate-$\kappa N$)$_2$ (Walsh & Hathaway, 1980). The terminal Zn2 atoms of the anionic fragments display a distorted tetrahedral $Cl_3N$ environment [Zn2—Cl = 2.2305 (7)–2.2658 (7) Å], which is similar to that observed for the anion in $(LH)[Zn(L)Cl_3]$ ($L$ = quinoline; Wang *et al.*, 2001). A few examples of charge-separated aquazinc(II)/trichlorozincate(II) arrays have been provided by organic *N*-donors such as urotropine (Mak &

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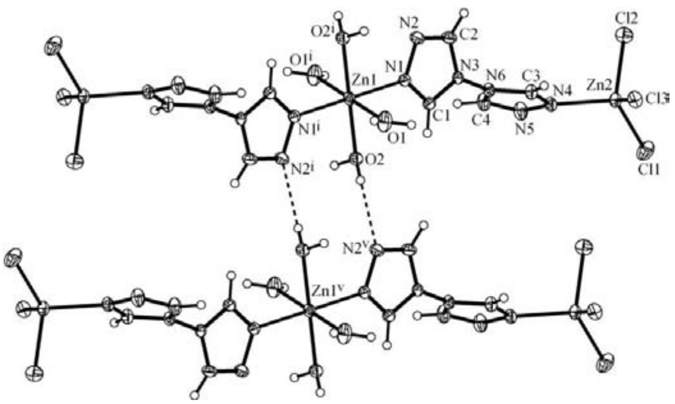

**Figure 1**
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x, -y, -z$; (v) $x - 1, y, z$.]

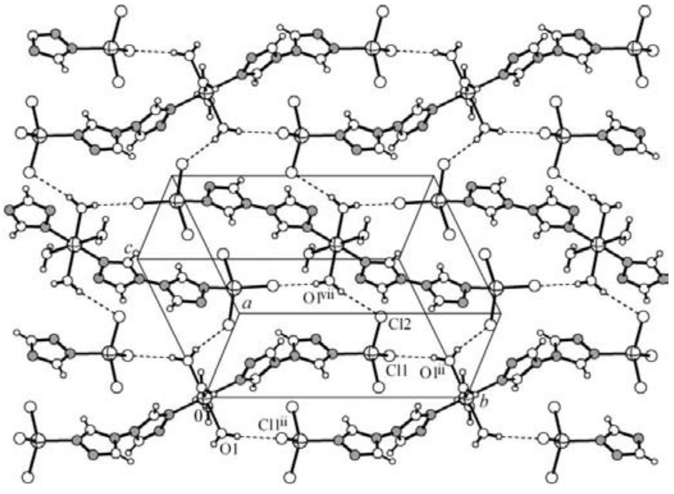

**Figure 2**
A fragment of the structure of (I), showing the packing mode of the long metal–organic molecules and their interconnection by O—H$\cdots$Cl hydrogen bonds. O2—H4*W*$\cdots$N2$^v$ hydrogen bonding expands the structure in the *a* direction, which is orthogonal to the plane of the drawing. [Symmetry codes: (ii) $-x, -y + 1, -z$; (v) $x - 1, y, z$; (vii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$.]

Huang, 1987) and 1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione (Jin *et al.*, 2005), but the zwitterionic trinuclear molecule of (I) has no counterpart in the chemistry of zinc(II) chloride and nonchelating nitrogen ligands.

The noncoordinated N atoms of the btr molecules of (I) participate in intermolecular O—H$\cdots$N hydrogen bonds, one type of which, *viz.* H4*W*$\cdots$N2$^v$ (see Table 2 for details), connects the molecular complexes into chains. In terms of the graph-set formalism (Etter *et al.*, 1990), pairs of such intermolecular interactions lead to ten-membered $R_2^2(10)$ rings translated parallel to the *a* axis (Fig. 1), while pairs of somewhat stronger H3*W*$\cdots$N5$^{iv}$ interactions link the molecules into layers parallel to the *bc* plane. Thus, the set of O—H$\cdots$N bonds leads to a three-dimensional array. The role of O—H$\cdots$Cl hydrogen bonds is also important. These intermolecular interactions generate a two-dimensional packing pattern, parallel to ($\bar{1}02$) (Fig. 2), employing four of the six available Cl atoms as hydrogen-bond acceptors. Pairs of weaker C—H$\cdots$Cl hydrogen bonds (Desiraju & Steiner, 1999) are observed between molecules related by inversion and, in total, the terminal $[ZnCl_3]^-$ units are involved in four hydrogen bonds.

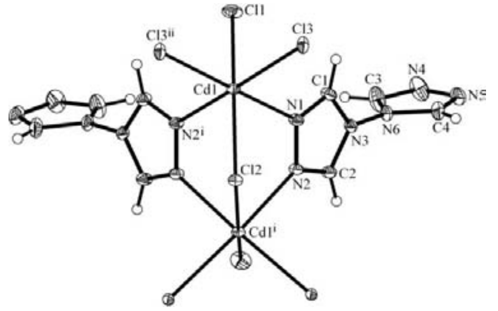

**Figure 3**
The structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $1 - x, -y, 2 - z$.]

The less polarizing $Cd^{2+}$ cation, as a weaker Lewis acid, forces the $Cl^-$ anions to behave as co-bridging linkers, resulting in the formation of the more complicated polymeric architecture observed in the structure of (II). The $N_2Cl_4$ coordination environment of the Cd1 ion is realized as a distorted octahedron comprising four bonds with $Cl^-$ anions [Cd1—Cl = 2.5869 (2)–2.6248 (7) Å], the lengths of which are typical of compounds with the same coordination environment (Villa *et al.*, 1971). The coordination is completed by N atoms of the organic ligand located in *cis* positions [Cd1—N = 2.386 (2) and 2.382 (2) Å]. Such a configuration of a $CdN_2Cl_4$ octahedron is uncommon among complexes with nonchelating *N*-donor ligands [*e.g.* Cd(piperazine)$Cl_2$; Vaidhyanathan *et al.*, 2003] (Fig. 3).

Both organic and inorganic ligands bridge the metal ions of (II) and contribute to the overall connectivity as complementary linkers. Thus, pairs of Cd ions are bridged by Cl2 [Cd1—Cl2—Cd1$^i$ = 98.25 (1)°; symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$] and two $N^1$,$N^2$-bidentate btr ligands similar to the pattern observed in $[\{Cd_3(\mu_2\text{-}L)_4(\mu_2\text{-}Cl)_2\}(\mu_2\text{-}NCS)_2(NCS)_2]\cdot 2H_2O$ (*L* = 4-amino-3,5-dimethyltriazole; Yi *et al.*, 2004), yielding the primary dinuclear unit of the structure. This coordination mode of the btr ligand is unprecedented; it behaves as a monofunctional triazole, leaving the second available trz ring noncoordinated. Interconnection of the dinuclear units occurs entirely *via* the $Cl^-$ ligands, which function as either single or double bridges between the Cd ions. Two Cl3 atoms act as double $\mu_2$-bridges between the $[Cd_2(\mu_2\text{-btr})_2(\mu_2\text{-Cl2})]^{3+}$ binuclear fragments [Cd1—Cl3—Cd1$^{ii}$ = 87.59 (2)°; symmetry code: (ii) $-x + 1, -y, -z + 2$] and assemble them into zigzag $[Cd_2(\mu_2\text{-btr})_2(\mu_2\text{-Cl2})(\mu_2\text{-Cl3})_2]_n^{n+}$ chains running parallel to the *c* axis, with a Cd1$\cdots$Cd1$^{ii}$ separation of 3.6210 (4) Å. The chains are connected into a two-dimensional coordination network parallel to the *bc* plane by means of Cl1 anions, which lie on inversion centres and supply unusual linear interlinks between the Cd ions [Cd1$\cdots$Cd1$^{vi}$ = 5.1737 (5) Å; symmetry code: (vi) $-x + 1$,

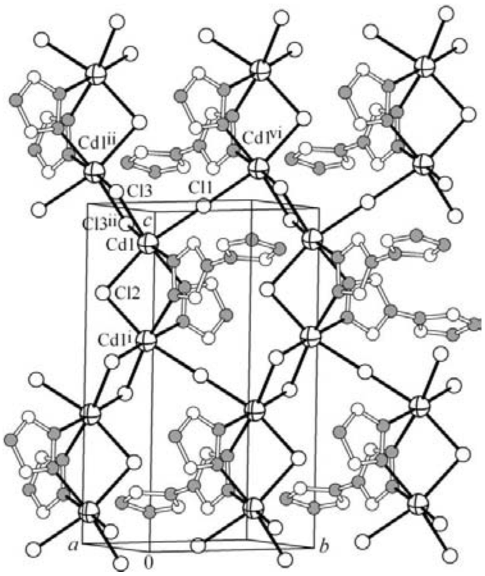

**Figure 4**
The two-dimensional network in the structure of (II), which is supported by a combination of inorganic (bold lines) and organic bridges. H atoms and part of the noncoordinated trz groups have been omitted for clarity. N atoms are shaded grey. [Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $1 - x, -y, 2 - z$; (vi) $-x + 1, -y + 1, -z + 2$.]

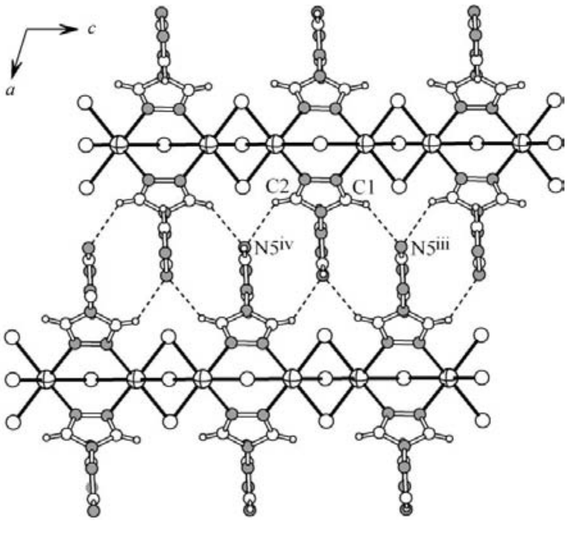

**Figure 5**
The packing of successive coordination layers in the structure of (II), showing interdigitation of the noncoordinated trz groups (projection on to the *ac* plane). Dashed lines indicate weak C—H$\cdots$N hydrogen bonds. [Symmetry codes: (iii) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + 2$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.]

$-y + 1, -z + 2$]; Cl2 atoms lie on twofold axes). This geometry at a bridging $Cl^-$ anion is rare; it has been observed for a few anionic complexes, such as $(MeNH_3)_2[CdCl_4]$ (Chapuis *et al.*, 1975). The successive coordination sheets are separated by 10.39 Å and their noncoordinated trz termini are interdigitated, supporting very weak interlayer C—H$\cdots$N hydrogen bonding (Table 4 and Fig. 5).

In conclusion, we have demonstrated how the structure of $M$Cl$_2$–btr coordination compounds depends upon the Lewis nature of the dication ($Zn^{2+}$ or $Cd^{2+}$). Co-operation of the bitriazole and $Cl^-$ bridges is relevant for the polymeric array adopted by soft $Cd^{2+}$ ions and this provides a paradigm for hybrid organic–inorganic structures of polyfunctional triazoles, whereas for strongly polarizing $Zn^{2+}$, the ligands are not complementary and produce two distinct coordination geometries within a zwitterionic molecular complex.

## Experimental

All materials were of reagent grade and were used as received. The btr ligand was prepared according to the reported procedure of Bartlett & Humphrey (1967). The title coordination compounds, (I) and (II), were synthesized in a similar manner. Evaporation of mixed aqueous solutions (3 ml) of $CdCl_2 \cdot H_2O$ (0.0402 g, 0.2 mmol) and btr (0.0136 g, 0.1 mmol) in a desiccator over $H_2SO_4$ for a few days afforded colourless prisms of (II) (yield 84%). Compound (I) was prepared in an analogous manner in 65% yield.

### Compound (I)

*Crystal data*

$[Zn_3Cl_6(C_4H_4N_6)_2(H_2O)_4]$
$M_r = 753.14$
Monoclinic, $P2_1/c$
$a = 6.8300$ (5) Å
$b = 14.6428$ (14) Å
$c = 12.5650$ (9) Å
$\beta = 104.903$ (9)°

$V = 1214.36$ (17) Å$^3$
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 3.64$ mm$^{-1}$
$T = 213$ (2) K
0.23 × 0.18 × 0.17 mm

*Data collection*

Stoe IPDS diffractometer
Absorption correction: part of the refinement model ($\Delta F$) (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.424$, $T_{\max} = 0.536$

10447 measured reflections
2849 independent reflections
2157 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.040$

**Table 1**
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.0930 (17) | Zn2—Cl1 | 2.2305 (7) |
| Zn1—O2 | 2.1091 (17) | Zn2—Cl2 | 2.2589 (7) |
| Zn1—O1 | 2.136 (2) | Zn2—Cl3 | 2.2658 (7) |
| Zn2—N4 | 2.0545 (18) | | |
| N1—Zn1—O2 | 87.67 (7) | N4—Zn2—Cl2 | 103.40 (6) |
| N1—Zn1—O1 | 92.25 (7) | Cl1—Zn2—Cl2 | 111.79 (3) |
| O2—Zn1—O1 | 88.31 (8) | N4—Zn2—Cl3 | 98.71 (6) |
| N4—Zn2—Cl1 | 116.35 (6) | Cl1—Zn2—Cl3 | 114.99 (3) |

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

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1—H1$W\cdots$Cl1$^{\text{ii}}$ | 0.80 (2) | 2.51 (2) | 3.294 (2) | 167 (3) |
| O1—H2$W\cdots$Cl2$^{\text{iii}}$ | 0.79 (2) | 2.55 (2) | 3.318 (2) | 163 (3) |
| O2—H3$W\cdots$N5$^{\text{iv}}$ | 0.81 (2) | 2.00 (2) | 2.809 (3) | 174 (3) |
| O2—H4$W\cdots$N2$^{\text{v}}$ | 0.80 (2) | 2.31 (3) | 2.976 (3) | 142 (4) |
| C2—H2$\cdots$Cl3$^{\text{vi}}$ | 0.94 | 2.62 | 3.445 (2) | 147 |
| C3—H3$\cdots$Cl2$^{\text{vi}}$ | 0.94 | 2.64 | 3.493 (3) | 151 |

Symmetry codes: (ii) $-x, -y + 1, -z$; (iii) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - 1, y, z$; (vi) $-x + 1, -y + 1, -z$.

**Table 3**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| Cd1—N1 | 2.382 (2) | Cd1—Cl3$^{ii}$ | 2.6154 (7) |
| Cd1—N2$^{i}$ | 2.386 (2) | Cd1—Cl3 | 2.6168 (8) |
| Cd1—Cl1 | 2.5869 (2) | Cd1—Cl2 | 2.6248 (7) |
| | | | |
| N1—Cd1—N2$^{i}$ | 83.24 (9) | Cl3$^{ii}$—Cd1—Cl3 | 92.41 (2) |
| N1—Cd1—Cl1 | 83.69 (6) | N1—Cd1—Cl2 | 85.56 (6) |
| N1—Cd1—Cl3$^{ii}$ | 174.19 (7) | Cl1—Cd1—Cl2 | 165.422 (19) |
| N1—Cd1—Cl3 | 91.18 (6) | Cl3—Cd1—Cl2 | 99.96 (2) |
| N2$^{i}$—Cd1—Cl3 | 171.48 (7) | Cd1—Cl2—Cd1$^{i}$ | 98.25 (4) |
| Cl1—Cd1—Cl3 | 90.10 (2) | Cd1$^{ii}$—Cl3—Cd1 | 87.59 (2) |

Symmetry codes: (i) $-x+1, y, -z+\frac{3}{2}$; (ii) $-x+1, -y, -z+2$.

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1···N5$^{iii}$ | 0.94 | 2.47 | 3.274 (4) | 144 |
| C2—H2···N5$^{iv}$ | 0.94 | 2.57 | 3.193 (4) | 124 |
| C4—H4···Cl3$^{v}$ | 0.94 | 2.81 | 3.531 (4) | 135 |

Symmetry codes: (iii) $-x+\frac{3}{2}, -y+\frac{3}{2}, -z+2$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+2$.

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.056$
$S = 0.89$
2849 reflections
167 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.76$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.63$ e Å$^{-3}$

## Compound (II)

*Crystal data*

$[CdCl_2(C_4H_4N_6)]$
$M_r = 319.43$
Monoclinic, $C2/c$
$a = 21.789$ (2) Å
$b = 6.3833$ (4) Å
$c = 13.8073$ (13) Å
$\beta = 107.468$ (11)°
$V = 1831.8$ (3) Å$^3$
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 2.93$ mm$^{-1}$
$T = 213$ (2) K
0.21 × 0.20 × 0.17 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.528$, $T_{\max} = 0.610$
6891 measured reflections
2179 independent reflections
1863 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.069$
$S = 0.99$
2179 reflections
120 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 2.76$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.67$ e Å$^{-3}$

For (I), O-bound H atoms were found in intermediate Fourier maps and were refined fully with isotropic displacement parameters and with restraints for the O—H bond lengths [O—H = 0.79 (2)–0.81 (2) Å]. For both structures, C-bound H atoms were treated as riding in geometrically idealized positions, with C—H = 0.94 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *IPDS Software* (Stoe & Cie, 2000) for (I); *SMART-NT* (Bruker, 1998) for (II). Cell refinement: *IPDS Software* for (I); *SAINT-NT* (Bruker, 1999) for (II). Data reduction: *IPDS Software* for (I); *SAINT-NT* for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3126). Services for accessing these data are described at the back of the journal.

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