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Bis(acetato-κ^2O,O')(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')-mercury(II) in two differently hydrated crystal forms

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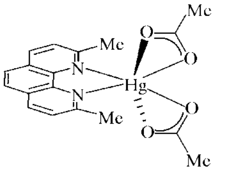
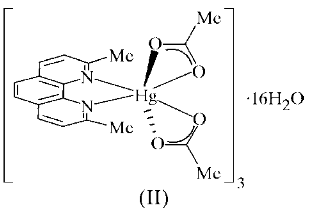
Two differently hydrated crystal forms of the title compound, *viz.* bis(acetato-κ^2O,O')(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')mercury(II), $[Hg(C_2H_3O_2)_2(C_{14}H_{12}N_2)]$ or $[HgAc_2(dmph)]$ [dmph is 2,3-dimethyl-1,10-phenantroline (neocuproine) and Ac is acetate], (I), and tris[bis(acetato-κ^2O,O')-(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')mercury(II)] hexadecahydrate, $[Hg(C_2H_3O_2)_2(C_{14}H_{12}N_2)]_3\cdot16H_2O$ or $[HgAc_2(dmph)]_3\cdot16H_2O$, (II), are presented. Both structures are composed of very simple monomeric units, which act as the building blocks of complex packing schemes stabilized by a diversity of π–π and hydrogen-bonding interactions.

Comment

The weak interactions responsible for the self-assembly of metal–organic systems have become the main topic of many structural reports, with the result that the molecular building blocks themselves end up being viewed as merely supporting media for these interactions to occur. The presence of water molecules and/or polycyclic aromatic ligands often sets favourable conditions for the appearance of these interactions. In these cases, the resulting complexes are usually prone to generating a variety of strong packing interactions, such as hydrogen bonds or medium-range contacts linking aromatic rings, either in a slipped or displaced stacking arrangement (hereinafter π–π) or in an edge(or point)-to-face conformation (C—H$\cdots\pi$) [for details, see Janiak (2000)].


(I)


(II)

We present here the two title mercury acetate complexes, $[HgAc_2(dmph)]$ [dmph is dimethyl-1,10-phenantroline (neocuproine) and Ac is acetate], (I), and $[HgAc_2(dmph)]_3\cdot16H_2O$, (II), which may well constitute such cases. By means of a simple and rather predictable monomeric unit, $[HgAc_2(dmph)]$, which both structures share as their elemental building block, two very different three-dimensional structures are built up, with an unusual number and diversity of packing interactions which are interesting from a structural point of view.

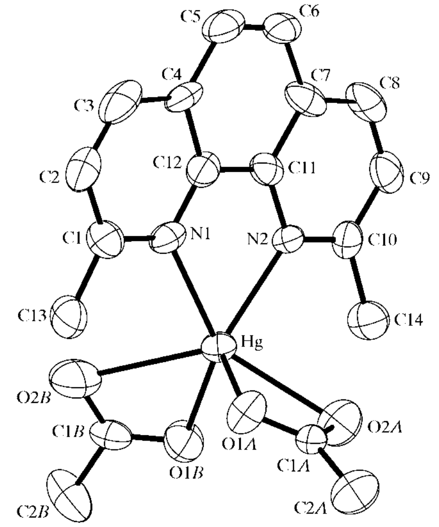


Figure 1
Molecular diagram for (I). Displacement ellipsoids are drawn at the 40% probability level. H atoms are not shown.

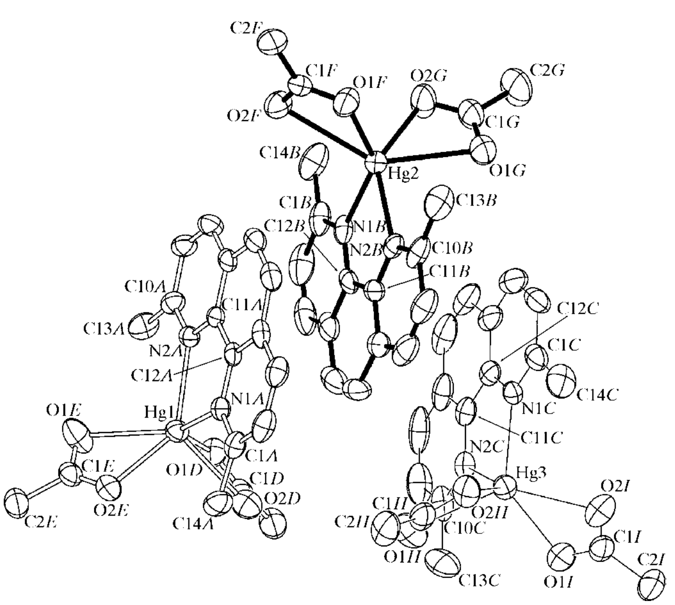


Figure 2
Molecular diagram for (II). Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted. For clarity, sequential atom labels C2*A*–C9*A*, C2*B*–C9*B* and C2*C*–C9*C* have been omitted.

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The monomeric building units in (I) and (II) are composed of an Hg^{2+} cation coordinated by three chelating ligands (one dmph and two acetate anions), providing an uneven six-coordinated environment for the cation. Due to the narrow bite of the ligands, the coordination polyhedra deviate from any regular geometry and the most adequate description is that of a square pyramid, in which atoms N1, N2, O1*A* and O1*B* define the base and the pair of atoms O1*B* and O2*B* occupy the apex. (In fact, the apical direction is represented by the C1*B*···Hg line.) In order to quantify these assertions, we quote here some values for structure (I), but these are representative of all four independent units: the mean deviation of atoms N1, N2, O1*A* and O1*B* from the best plane is 0.039 (1) Å, with the cation displaced 1.05 (1) Å from the plane towards the apex, and the deviation of the C1*B*···Hg line from the base normal is 7.9 (1)°.

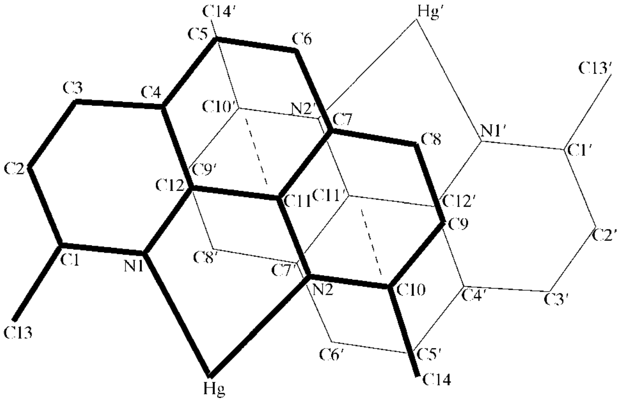
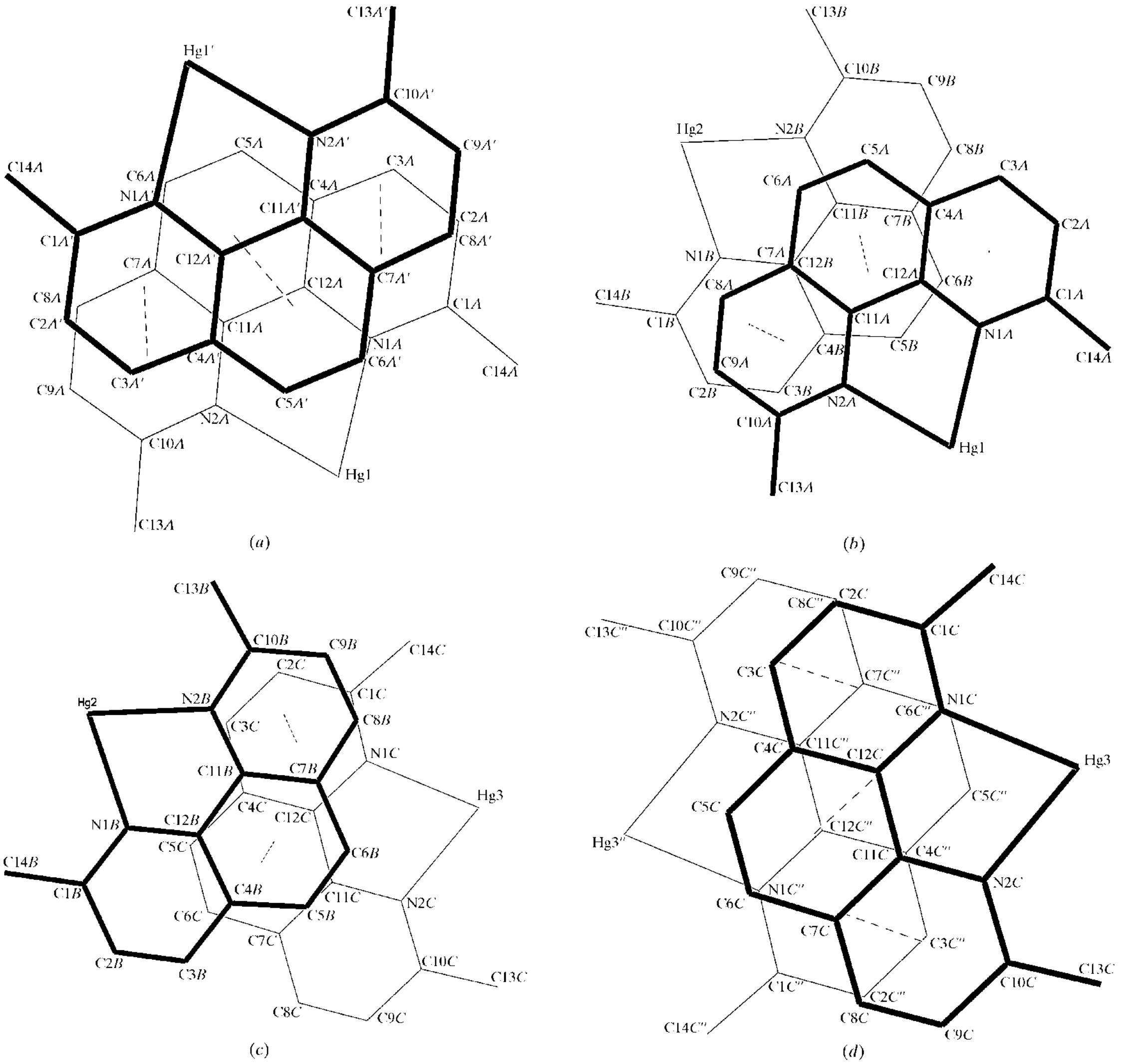


Figure 3
A schematic diagram showing the π–π interactions between dmph groups in (I). Primed labels denote atoms at the symmetry position (−*x*, 1 − *y*, 1 − *z*).

While this molecular unit is the only motif present in (I), the asymmetric unit of (II) is composed of three independent such [$HgAc_2$(dmph)] groups complemented by 16 hydration water molecules, for which the description of the intermolecular interactions becomes much more complex.

Inspection of Figs. 1 and 2, which present the four independent [$HgAc_2$(dmph)] units in both structures, confirms



(*a*)

(*b*)

(*c*)

(*d*)

Figure 4
Schematic diagrams showing the π–π interactions between dmph groups in (II). (*a*) The *A*′–*A* interaction, with primed labels denoting atoms at the symmetry position (2 − *x*, 1 − *y*, 2 − *z*); (*b*) the *A*–*B* interaction; (*c*) the *B*–*C* interaction; (*d*) the *C*–*C*″ interaction, with doubly primed labels denoting atoms at the symmetry position (2 − *x*, 1 − *y*, 1 − *z*).

their topological similarity. There remain, however, some geometric differences which might well have to do with packing processes (see below) and which can be analysed from the values in Tables 1 and 3, where surveys of relevant bond distances and angles around the cations are presented. In order to facilitate the comparison of homologous parameters, they have been grouped so that they appear in the list in the same sequence.

The dmph ligand binds, as usual, in a very symmetric fashion. The maximum difference in bond lengths corresponds to structure (II), where the difference in Hg—N distances is approximately twice the sum of the individual s.u. values, the remainder not being significant. In all four cases, the coordination plane through the cation is almost coincident with the ligand plane, with a maximum deviation of 2.1 (1)° displayed in structure (I).

All four cations [one in (I) and three in (II)] are coordinated by two acetate groups behaving quite differently. One of them binds symmetrically [unit *A* in (I), and units *D*, *G* and *I* in (II)], the other [unit *B* in (I), and units *E*, *F* and *H* in (II)] being asymmetric and presenting, in all cases but unit *H*, both the shortest as well as the longest coordination distances, with some of these last even being beyond normally accepted coordination distances [*viz*. Hg2—O2*F* = 2.752 (5) Å, compared with the *SHELXL*97 (Sheldrick, 1997) default value of 2.66 Å].

The extreme availability in both structures of pyridyl and aryl cycles prone to forming π–π contacts, and the large number of water molecules able to participate in hydrogen-bonding [in structure (II)] lead to very rich interaction schemes for these two compounds.

In structure (I), the main interaction present is the π–π bond shown in Fig. 3, which links the monomeric [Hg(dmph)Ac$_2$] building-block units into 'dimers', which are in fact the real structural motifs (Table 2). These units are in turn isolated in space, their interaction being much weaker and achieved through diffuse van der Waals forces.

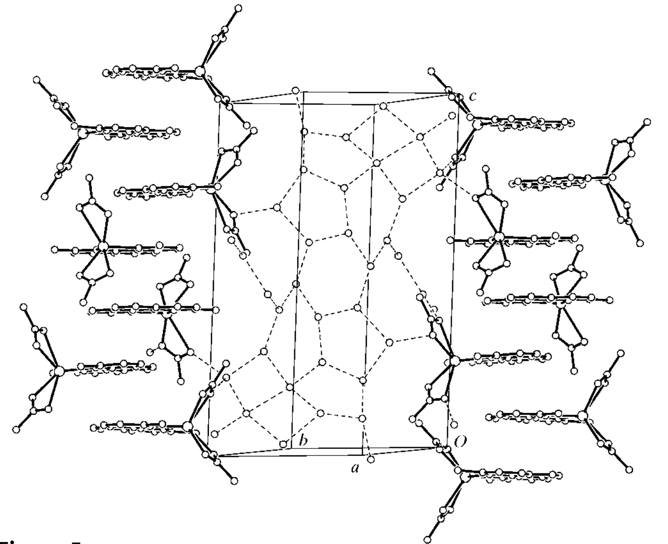


Figure 5
A packing view of (II) down the ($\overline{1}$10) direction, showing two columns connected by a dense network of crystallization water molecules. The columns one level above and below the water network (which complete a four-column environment of the water network) have been omitted for clarity.

Structure (II) can be described as chains of π–π-bonded monomers piled up on top of one another and aligned along the *c* axis, interlinked by a dense network of hydrogen-bonded water molecules. Monomers stack in the column in the sequence *CBA.ABC.CBA*, where the dot (.) denotes a symmetry centre and *A*, *B* and *C* represent the suffixes characterizing the aromatic ligands in each monomer. Thus, there are four different types of π–π contacts, which can be represented (using the above coding) as *A.A*, *AB*, *BC* and *C.C*. These are sketched in Fig. 4 and the relevant parameters are given in Table 4.

The columns thus formed are connected to each other *via* a hydrogen-bond network, which could be deduced from the O-atom positions as it was not possible to locate water H atoms with any degree of confidence in the presence of Hg. In spite of this limitation, the linkages are very clear, as shown in Fig. 5. All water H atoms take part in this hydrogen-bond network, with O$\cdots$O separations in the range 2.439 (17)–2.985 (17) Å.

Experimental

Compound (I) was prepared by direct mixing of a methanolic solution of Hg acetate and neocuproine with an aqueous solution of potassium persulfate, in such a way as to have 0.025 *M* final concentrations for all reagents. The solid material obtained after a few days was recrystallized from dimethylformamide, yielding pale-yellow prisms. Compound (II) was prepared by diffusion of an aqueous solution of potassium sulfate into a methanolic solution of Hg acetate and neocuproine through a very thin capillary initially full of water (all reagents in 0.025 *M* concentration). After a couple of days, pale-yellow prisms suitable for X-ray diffraction were obtained. The overwhelming number of crystallization water molecules in (II) renders the structure quite unstable at room temperature, to the extent that a single crystal usually survives just a few seconds under ambient conditions before collapsing. Sealed in a capillary with a drop of mother liquor, however, they can remain unaltered for weeks.

Compound (I)

Crystal data

$[Hg(C_2H_3O_2)_2(C_{14}H_{12}N_2)]$
$M_r = 526.93$
Triclinic, $P\overline{1}$
$a = 8.3619$ (15) Å
$b = 9.4973$ (18) Å
$c = 12.349$ (2) Å
$\alpha = 83.167$ (3)°
$\beta = 76.646$ (4)°
$\gamma = 66.027$ (3)°
$V = 871.5$ (3) Å^3

$Z = 2$
$D_x = 2.008$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 187 reflections
$\theta = 2.0$–25.0°
$\mu = 8.86$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.25 × 0.14 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996) in *SAINT* (Bruker, 2000)]
$T_{min} = 0.22$, $T_{max} = 0.41$
7356 measured reflections

3659 independent reflections
1839 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 28.0°$
$h = -10 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.084$
$S = 0.81$
3659 reflections
230 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0119P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}

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

Hg—O1*B*	2.188 (6)	Hg—O1*A*	2.380 (6)
Hg—N1	2.303 (7)	Hg—O2*A*	2.486 (7)
Hg—N2	2.310 (7)	Hg—O2*B*	2.723 (8)
N1—Hg—N2	72.1 (3)	O1*B*—Hg—O2*B*	50.3 (2)
O1*A*—Hg—O2*A*	52.9 (2)		

Table 2
π–π contacts for (I).

Group 1/Group 2	IPD (Å)	CCD (Å)	SA (°)
C4–C7,C11,C12/N1′,C1′–C4′,C12′	3.46 (1)	3.62 (1)	18.2 (2)

Notes: see Fig. 3 for details of the atom labelling and symmetry code; IPD is the interplanar distance, CCD is the centre-to-centre distance and SA is the slippage angle.

Compound (II)

Crystal data

$[Hg(C_2H_3O_2)_2(C_{14}H_{12}N_2)]_3\cdot16H_2O$
$M_r = 1869.03$
Triclinic, $P\overline{1}$
$a = 13.738$ (3) Å
$b = 14.076$ (3) Å
$c = 20.615$ (4) Å
$\alpha = 93.11$ (3)°
$\beta = 90.85$ (3)°
$\gamma = 118.93$ (3)°
$V = 3480.2$ (16) Å^3

$Z = 2$
$D_x = 1.784$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 277 reflections
$\theta = 2.3$–23.8°
$\mu = 6.68$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.18 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan [*SADABS* (Sheldrick, 1996) in *SAINT* (Bruker, 2000)
$T_{\min} = 0.31$, $T_{\max} = 0.45$
29 254 measured reflections

14 989 independent reflections
9362 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 28.0°$
$h = -17 \rightarrow 17$
$k = -18 \rightarrow 17$
$l = -26 \rightarrow 26$

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

Hg1—O2*E*	2.256 (6)	Hg2—N2*B*	2.309 (5)
Hg1—N2*A*	2.306 (5)	Hg2—O1*G*	2.626 (6)
Hg1—N1*A*	2.313 (5)	Hg2—O2*F*	2.752 (5)
Hg1—O1*D*	2.384 (5)	Hg3—O1*I*	2.285 (6)
Hg1—O2*D*	2.529 (6)	Hg3—N2*C*	2.305 (6)
Hg1—O1*E*	2.547 (6)	Hg3—N1*C*	2.307 (5)
Hg2—O1*F*	2.197 (5)	Hg3—O2*H*	2.310 (5)
Hg2—N1*B*	2.282 (6)	Hg3—O2*I*	2.518 (6)
Hg2—O2*G*	2.291 (6)	Hg3—O1*H*	2.637 (7)
N1*A*—Hg1—N2*A*	72.51 (19)	O1*F*—Hg2—O2*F*	50.45 (18)
O1*D*—Hg1—O2*D*	52.0 (2)	N1*C*—Hg3—N2*C*	73.0 (2)
O1*E*—Hg1—O2*E*	51.8 (2)	O1*I*—Hg3—O2*I*	52.6 (2)
N1*B*—Hg2—N2*B*	73.2 (2)	O1*H*—Hg3—O2*H*	50.7 (2)
O1*G*—Hg2—O2*G*	50.0 (2)		

Table 4
π–π contacts for (II).

Group 1/Group 2	IPD (Å)	CCD (Å)	SA (°)
N2*A*′,C7*A*′–C11*A*′/N1*A*,C1*A*–C4*A*,C12*A*	3.40 (1)	3.60 (1)	19.2 (2)
C4*A*′–C7*A*′,C11*A*′,C12*A*′/C4*A*–C7*A*,C11*A*,C12*A*	3.39 (1)	3.67 (1)	22.4 (2)
N2*A*,C7*A*–C11*A*/N1*B*,C1*B*–C4*B*,C12*B*	3.45 (1)	3.51 (1)	21.0 (2)
C4*A*–C7*A*,C11*A*,C12*A*/C4*B*–C7*B*,C11*B*,C12*B*	3.45 (1)	3.55 (1)	13.7 (2)
N2*B*,C7*B*–C11*B*/N1*C*,C1*C*–C4*C*,C12*C*	3.45 (1)	3.54 (1)	13.1 (2)
C4*B*–C7*B*,C11*B*,C12*B*/C4*C*–C7*C*,C11*C*,C12*C*	3.43 (1)	3.51 (1)	10.7 (2)
N2*C*,C7*C*–C11*C*/N1*C*″,C1*C*″–C4*C*″,C12*C*″	3.42 (1)	3.64 (1)	20.2 (2)
C4*C*–C7*C*,C11*C*,C12*C*/C4*C*″–C7*C*″,C11*C*″,C12*C*″	3.43 (1)	3.68 (1)	22.4 (2)

Notes: see Fig. 4 for details of the atom labelling and symmetry codes; IPD is the interplanar distance, CCD is the centre-to-centre distance and SA is the slippage angle.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.114$
$S = 1.01$
14 989 reflections
820 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.010$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.77$ e Å^{-3}

Aromatic H atoms were placed at calculated positions (C—H = 0.93 Å) and allowed to ride on their parent atoms, while those of the terminal methyl groups were not included in the models because they could not be confidently positioned. A similar situation arose with the H atoms of the water molecules, which could not be reliably located in the presence of Hg, so they were disregarded from the model and the hydrogen-bonding interactions were discussed solely in terms of O···O distances. Full use of the CCDC package was made for searching the Cambridge Structural Database (Allen, 2002).

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTLPC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1012). Services for accessing these data are described at the back of the journal.

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