metal-organic compounds

catena-Poly[[bis(μ₂-4-methylbenzoato-κ²O:O′)disilver(I)(Ag—Ag)]-μ₂-di-2-pyridylamine-κ²N²:N²′] and *catena*-poly[[(di-2-pyridylamine-κN²)-(μ₂-4-nitrobenzoato-κ²O:O′)disilver(I)-(Ag—Ag)]-μ₃-4-nitrobenzoato-κ³O:O′:O′]

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Both title compounds are polynuclear polymeric complexes with binuclear units. In the former compound, $[Ag_2(C_8H_7O_2)_2(C_{10}H_9N_3)]_n$, the two Ag^I atoms display distorted square-planar coordinations. This compound contains a twofold axis and a crystallographic inversion centre, and di-2-pyridylamine (DPA) ligands crosslink adjacent binuclear units to form infinite polymeric chains. Crystal packing is stabilized by van der Waals interactions and partial π–π stacking interactions between the chains. The latter compound, $[Ag_2(C_7H_4NO_4)_2(C_{10}H_9N_3)]_n$, contains crystallographic inversion centres and the two Ag^I atoms exhibit two types of distorted square-pyramidal coordination. Ag—Ag argentophilic interactions and Ag—O crosslinking between adjacent binuclear units contribute to form infinite polymeric chains. Weak π–π stacking interactions are observed in the polymer chain. Crystal packing is stabilized by C—H···O hydrogen bonds and by weak π–π stacking interactions.

Comment

Ag^I—N and Ag^I—O bonding complexes are potential bioinorganic materials (Clement & Jarrett, 1994; Russell & Hugo, 1994; Shaw, 1999; Feng *et al.*, 2000; Gimeno & Laguna, 2004). Nomiya *et al.* (2004) reported that dimeric or polymeric Ag^I—O bonding complexes show a wide range of antimicrobial activities. Kasuga *et al.* (2006) synthesized a polymeric light-stable and water-soluble Ag^I—O bonding complex, and demonstrated its antimicrobial activity against selected bacteria, yeasts and moulds. The aim of this study is to synthesize a new type of antimicrobial Ag^I–benzoate complex. We report here the crystal structures of the title polynuclear polymeric complexes with dinuclear units, the former, (I),

being made up of di-2-pyridylamine (DPA) and *p*-toluic acid (TA), with the electron-donating methyl group, and the latter, (II), being comprised of DPA and *p*-nitrobenzoic acid (NA), with the electron-attracting nitro group.

(I)

(II)
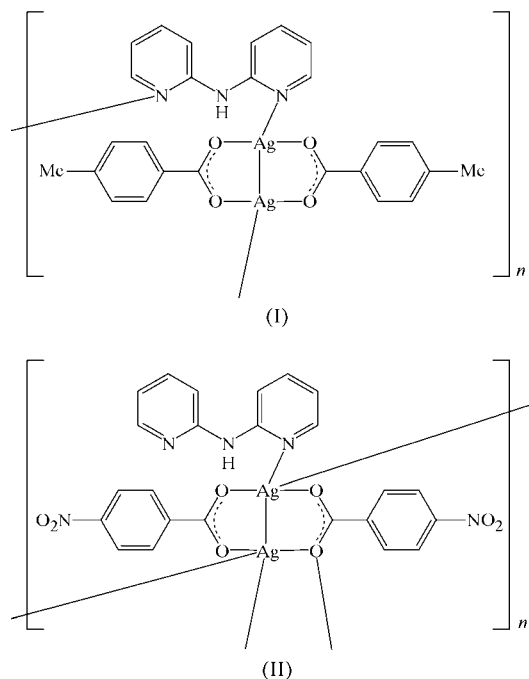
The structure of (I) is shown to be a binuclear complex, which is composed of two Ag^I atoms, one DPA ligand and two TA ligands (Fig. 1). Selected geometric parameters are given in Table 1. The two halves of DPA are related by a twofold axis which passes through the central secondary amino group, N2—H22. Also, a crystallographic inversion centre is located at $(\frac{1}{2}, \frac{1}{2}, 1)$, *i.e.* at the centre of the Ag1—Ag1^i bond vector [symmetry code: (i) $1 - x$, $1 - y$, $2 - z$]. The Ag1 atom is coordinated by Ag1^i, pyridyl atom N1 from DPA and carboxyl atoms O1 and O2^i from two TA ligands. The Ag1—Ag1^i distance (Table 1) is approximately equal to that of metallic
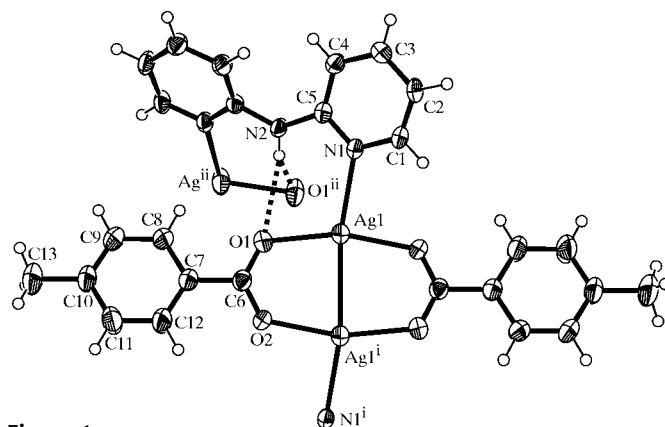
Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by symmetry operation (i) for NA and (ii) for DPA. Dashed lines indicate the bifurcated hydrogen bond. [Symmetry codes: (i) $1 - x$, $1 - y$, $2 - z$; (ii) $1 - x$, y, $\frac{3}{2} - z$.]

silver (2.886 Å), indicating an apparent Ag—Ag metal bond (Zheng *et al.*, 2003; Zhu *et al.*, 2003; Tang *et al.*, 2004; You *et al.*, 2004). The chelating atoms form a distorted square-planar coordination geometry around Ag1 (r.m.s. deviation of fitted atoms = 0.1651 Å).

DPA crosslinks adjacent binuclear units to form infinite zigzag polymer chains along the *c* axis (Fig. 2), with the pyridine ring of DPA (C1–C5/N1) tilted from the coordination plane (Ag1/Ag1^i/N1/O1/O2^i) by 17.2 (1)°, and with the two halves of DPA twisting about the central N2—H22 bond by 33.7 (1)°. In the polymer chain, bifurcated hydrogen bonds are present, namely N2—H22···O1 and N2—H22···O1^{ii} [symmetry code: (ii) $1 - x, y, \frac{3}{2} - z$] (Fig. 1 and Table 2).

The crystal packing of (I) is stabilized by van der Waals interactions between the TA ligands of neighbouring polymer chains, with C9···C13^{iii} and C13···C9^{iii} distances of 3.541 (8) Å [symmetry code: (iii) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$]. A partial π–π stacking interaction is also observed between adjacent parallel pyridine rings of DPA (Fig. 3 and Table 3).

The structure of (II) is shown in Fig. 4 and selected geometric details are given in Table 4. The pyridine rings of DPA, *viz*. C1–C5/N1 and C6–C10/N3, and the benzene rings of NA, *viz*. C12–C17 and C19–C24, are defined as rings *A*, *B*, *C*

Figure 2
A view of the core structure of (I), comprised of DPA, Ag1 and chelating atoms, showing the polymer chain along the *c* axis. H atoms have been omitted for clarity.

Figure 3
The crystal packing of the core structure of (I). Dashed lines indicate the partial π–π stacking interactions between the pyridine rings of DPA. H atoms have been omitted for clarity.

and *D*, respectively. As in (I), the unit complex in (II) is composed of two Ag^I atoms, one DPA ligand and two NA ligands, forming the binuclear complex. However, in (II), two types of slightly distorted square-pyramidal geometries are present. The Ag1 atom is coordinated by pyridyl atom N1 from DPA, carboxyl atoms O1 and O6 from two NA ligands and atom Ag2 in the basal plane (r.m.s. deviation of fitted atoms = 0.1804 Å), and the apical site of the pyramid is occupied by Ag2^v [symmetry code: (v) $2 - x, -y, 1 - z$]. However, the Ag2 atom is not coordinated by N. The Ag2 atom is coordinated by carboxyl atoms O2 and O5 from two NAs, atom O5^{vi} from NA of an adjacent binuclear unit [symmetry code: (vi) $3 - x, -y, 1 - z$] and atom Ag1 in the basal plane (r.m.s. deviation of fitted atoms = 0.1328 Å), and atom Ag1^v occupies the apical site of the pyramid. There is an intramolecular N2—H22···O6 hydrogen bond (Fig. 4 and Table 5).

The Ag1—Ag2 distance in the coordination basal plane (Table 4) indicates an apparent Ag—Ag metal bond. The axial Ag1—Ag2^v (= Ag2—Ag1^v) distance of the pyramids (Table 4) is shorter than the sum of the van der Waals radii of two Ag^I atoms (3.44 Å), and longer than the Ag—Ag metal bond. This may suggest that they are related by what has been referred to as argentophilicity (Kaltsoyannis, 1997; Tang *et al.*, 2004). Argentophilic interactions crosslink two binuclear units along the axial direction of the pyramids, and Ag2—O5^{vi} and O5—Ag2^{vi} crosslink adjacent binclear units along the *a* axis. Consequently, the overall structure of (II) is formed into an infinite polymer chain complex along the *a* axis (Fig. 5). The *A* and *B* rings of DPA are tilted from each other by 16.7 (2)°, and two NAs are twisted at C11—C12 and C18—C19 by 29.6 (2) and by 10.5 (3)°, respectively, to avoid steric hindrance caused by polymerization. In the polymer chain of (II), crystallographic inversion centres are located at $(1, 0, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$. Crystal packing is stablized by C—H···O interactions between polymer chains (Table 5). Weak π–π stacking interactions are observed between several adjacent six-membered
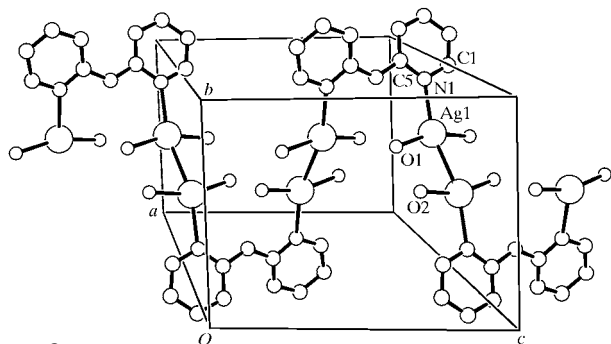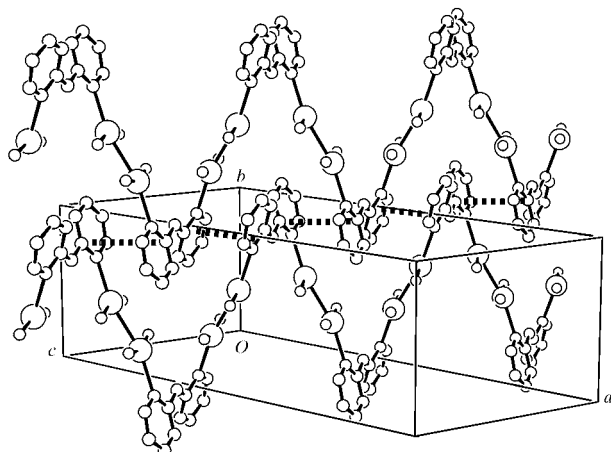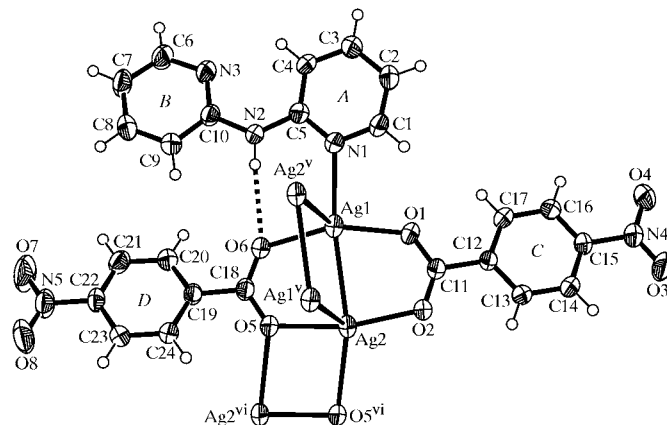

Figure 4
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the intramolecular hydrogen bond. [Symmetry codes: (v) $2 - x, -y, 1 - z$; (vi) $3 - x, -y, 1 - z$.]

rings, including rings *C* and *D*, an interaction which is along the axial direction of the coordination pyramid (Fig. 6 and Table 6).

In the present study, two types of ligands are chosen, namely TA with the electron-donating methyl group and NA with the electron-attracting nitro group. Coordination geometries in both compounds are very similar, with Ag^I—O bond lengths ranging from 2.180 (3) to 2.214 (3) Å. In previously reported crystal structures of dimeric or polymeric Ag^I complexes containing benzoic acid or its derivatives as ligands, Ag^I—O bond lengths range from 2.175 to 2.302 Å (Usubaliev *et al.*, 1981; Hedrich & Hartl, 1983; Smith *et al.*, 1988; Movsumov *et al.*, 1990; Mak *et al.*, 1993; Smith *et al.*, 1994; Ülkü *et al.*, 1996; Jian *et al.*, 2004; You *et al.*, 2004; Wang & Okabe, 2005), which are comparable with those of the present complexes. This suggests that the coordination strengths of Ag^I—O bonds are unaffected by the properties of methyl and nitro substituents at the *para* position of benzoic acid.

Experimental

All procedures were carried out at room temperature. For the synthesis of compound (I), a solution of $AgNO_3$ (2.5 mg, 0.015 mmol) in H_2O (0.1 ml) was added to a solution of di-2-pyridylamine (5 mg, 0.032 mmol) in dimethylformamide (DMF) (1 ml) and the mixture was stirred for 10 min. *p*-Toluic acid (3.9 mg, 0.029 mmol) dissolved in DMF (1 ml) was added to this solution and the mixture was stirred for 30 min. After evaporation for 10 d at room temperature, colourless platelet crystals were formed. For the synthesis of compound (II), a solution of $AgNO_3$ (1.25 mg, 0.008 mmol) in H_2O (0.1 ml) was added to a solution of di-2-pyridylamine (2.5 mg, 0.016 mmol) in MeOH–H_2O (90% *v/v*, 3 ml) and the mixture was stirred for 10 min. *p*-Nitrobenzoic acid (2.4 mg, 0.014 mmol) dissolved in DMF (1 ml) was added to this solution and the mixture was stirred for 30 min. After evaporation for 5 d, colourless platelet crystals crystallized from the mixture.
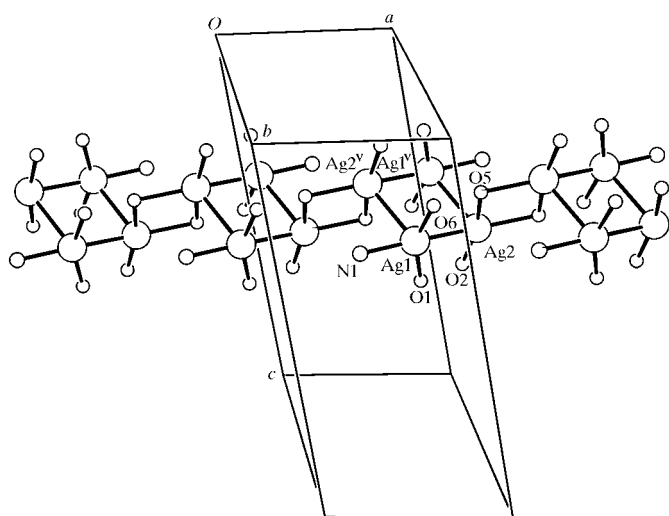

Figure 5
The crystal packing of the core structure of (II), comprised of Ag1, Ag2 and the chelating atoms, showing the polymer chain along the *a* axis. [Symmetry code: (v) $2 - x, -y, 1 - z$.]
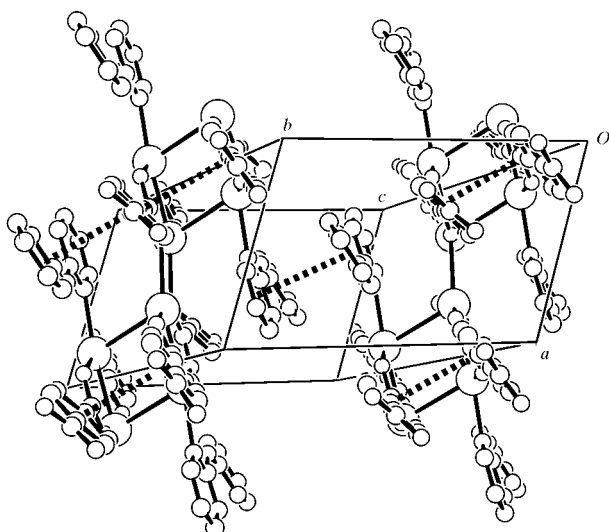
Figure 6
The crystal packing of (II). Dashed lines indicate weak π–π stacking interactions. H atoms have been omitted for clarity.

Compound (I)

Crystal data

$[Ag_2(C_8H_7O_2)_2(C_{10}H_9N_3)]$	$Z = 4$
$M_r = 657.21$	$D_x = 1.859$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 24.76$ (2) Å	$\mu = 1.71$ mm^{-1}
$b = 8.59$ (1) Å	$T = 296.1$ K
$c = 11.55$ (1) Å	Platelet, colourless
$\beta = 107.11$ (3)°	$0.20 \times 0.10 \times 0.03$ mm
$V = 2348$ (4) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	11540 measured reflections
ω scans	2679 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	1585 reflections with $F^2 > 2\sigma(F^2)$
$T_{min} = 0.639$, $T_{max} = 0.949$	$R_{int} = 0.048$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2]$
$wR(F^2) = 0.058$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.80$	$(\Delta/\sigma)_{max} = 0.001$
2679 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.79$ e Å^{-3}

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

Ag1—O1	2.179 (3)	Ag1—N1	2.401 (4)
Ag1—O2^i	2.203 (3)	Ag1—Ag1^i	2.833 (3)
O1—Ag1—O2	162.05 (9)	O1—Ag1—Ag1^i	84.41 (8)
O1—Ag1—N1	106.07 (9)	O2—Ag1—Ag1^i	78.87 (7)
O2—Ag1—N1	91.64 (9)	N1—Ag1—Ag1^i	164.49 (6)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H22$\cdots$O1	0.86	2.48	3.197 (5)	141

Table 3
π–π stacking interactions (Å, °) in the crystal packing of (I).

Cg is the centroid of the C1–C5/N ring.

CgI	CgJ	$Cg\cdots Cg$	Interplanar angle	CgI-perp	CgJ-perp	Slippage
Cg	Cg^{iv}	3.919 (5)	0.00	3.352	3.352	2.030

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

Compound (II)

Crystal data

[Ag₂(C₇H₄NO₄)₂(C₁₀H₉N₃)]
$M_r = 719.17$
Triclinic, $P\bar{1}$
$a = 7.259$ (8) Å
$b = 11.07$ (1) Å
$c = 15.38$ (2) Å
$\alpha = 82.66$ (5)°
$\beta = 84.84$ (4)°
$\gamma = 72.01$ (4)°

$V = 1164$ (2) Å³
$Z = 2$
$D_x = 2.051$ Mg m⁻³
Mo $K\alpha$ radiation
$\mu = 1.75$ mm⁻¹
$T = 296.1$ K
Platelet, colourless
$0.40 \times 0.20 \times 0.03$ mm

Data collection

Rigaku R-AXIS RAPID
    diffractometer
ω scans
Absorption correction: multi-scan
    (*ABSCOR*; Higashi, 1995)
    $T_{min} = 0.582$, $T_{max} = 0.957$

11341 measured reflections
5281 independent reflections
4093 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.088$
$S = 1.01$
5281 reflections
351 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.06$ e Å⁻³
$\Delta\rho_{min} = -0.79$ e Å⁻³

Table 4
Selected geometric parameters (Å, °) for (II).

Ag1—O6	2.187 (3)	Ag1—Ag2�v	3.158 (2)
Ag1—O1	2.194 (3)	Ag2—O2	2.183 (3)
Ag1—N1	2.353 (3)	Ag2—O5	2.214 (3)
Ag1—Ag2	2.855 (3)	Ag2—O5�vi	2.626 (4)
O6—Ag1—O1	153.23 (9)	O2—Ag2—O5	167.26 (8)
O6—Ag1—N1	107.18 (10)	O2—Ag2—Ag1	84.96 (8)
O1—Ag1—N1	95.94 (9)	O5—Ag2—Ag1	82.33 (8)
O6—Ag1—Ag2	81.16 (9)	O2—Ag2—Ag1�v	101.48 (10)
O1—Ag1—Ag2	77.11 (7)	O5—Ag2—Ag1�v	73.65 (10)
N1—Ag1—Ag2	170.57 (6)	Ag1—Ag2—Ag1�v	71.45 (7)
O6—Ag1—Ag2�v	83.11 (10)	O2—Ag2—O5�vi	109.31 (9)
O1—Ag1—Ag2�v	118.55 (9)	O5—Ag2—O5�vi	83.30 (9)
N1—Ag1—Ag2�v	68.95 (9)	Ag1—Ag2—O5�vi	161.49 (5)
Ag2—Ag1—Ag2�v	108.55 (7)		

Symmetry codes: (v) $-x + 2, -y, -z + 1$; (vi) $-x + 3, -y, -z + 1$.

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H22$\cdots$O6	0.86	2.37	3.220 (5)	168
C6—H6$\cdots$O1ᵛⁱⁱ	0.93	2.65	3.394 (5)	138
C7—H7$\cdots$O8ᵛⁱⁱⁱ	0.93	2.60	3.316 (5)	134
C14—H14$\cdots$O7ⁱˣ	0.93	2.55	3.404 (6)	154
C23—H23$\cdots$O4ˣ	0.93	2.65	3.372 (5)	135

Symmetry codes: (vii) $-x + 1, -y + 1, -z + 1$; (viii) $-x + 2, -y + 1, -z$; (ix) $x, y - 1, z + 1$; (x) $x + 1, y, z - 1$.

Table 6
π–π stacking interactions (Å, °) in the crystal packing of (II).

CgA, CgB, CgC and CgD are the centroids of rings C1–C5/N1 (*A*), C6–C10/N3 (*B*), C12–C17 (*C*) and C19–C24 (*D*), respectively.

CgI	CgJ	$Cg\cdots Cg$	Interplanar angle	CgI-perp	CgJ-perp	Slippage
CgA	CgB^{vii}	3.750 (5)	16.73	3.520	3.671	1.065
CgB	CgD^{xi}	3.697 (5)	12.75	3.394	3.617	1.176
CgC	CgC^{xii}	3.914 (5)	0.00	3.479	3.479	1.792
CgC	CgD^{v}	3.746 (5)	8.96	3.432	3.552	1.356

Symmetry codes: (v) $-x + 2, -y, -z + 1$; (vii) $-x + 1, -y + 1, -z + 1$; (xi) $x - 1, y, z$; (xii) $2 - x, -y, 2 - z$.

For both compounds, all H atoms were located in difference Fourier maps and were then placed in idealized positions and treated as riding, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic H atoms, N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(N) for secondary amino H atoms, and C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. For compound (I), the methyl H atoms were additionally allowed to rotate about the parent C—C bond. In compound (I), the highest maximum residual electron density is 0.62 Å from Ag1 and the deepest hole is 1.03 Å from Ag1. In compound (II), the corresponding peak and trough are 0.93 Å from Ag1 and 0.83 Å from Ag1, respectively.

For both compounds, data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *Crystal-Structure* (Rigaku/MSC, 2005) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *CrystalStructure*.

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