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# The dinuclear copper(II) complexes di-$\mu$-chlorido-bis{[*N*,*N*′-bis(4-chlorobenzyl)propane-1,2-diamine]chloridocopper(II)} and di-$\mu$-chlorido-bis{[*N*,*N*′-bis(3,4-methylenedioxybenzyl)propane-1,2-diamine]chloridocopper(II)}

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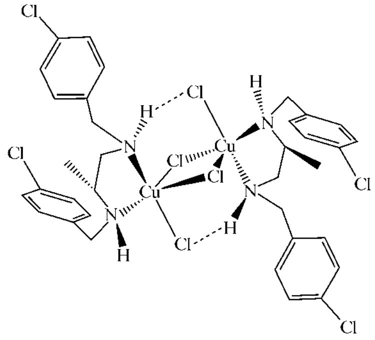
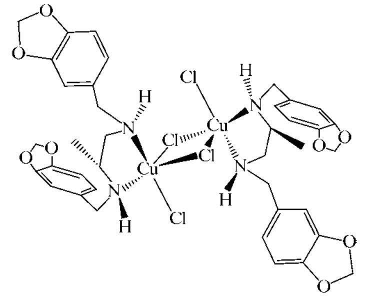
The two title dinuclear copper(II) complexes, $[Cu_2Cl_4(C_{17}H_{20}Cl_2N_2)_2]$, (I), and $[Cu_2Cl_4(C_{19}H_{22}N_2O_4)_2]$, (II), have similar coordination environments. In each complex, the asymmetric unit consists of one half-molecule and the two copper centres are bridged by a pair of Cl atoms, resulting in complexes with centrosymmetric structures containing Cu($\mu$-Cl)$_2$Cu parallelogram cores; the Cu$\cdots$Cu separations and Cu—Cl—Cu angles are 3.4285 (8) Å and 83.36 (3)°, respectively, for (I), and 3.565 (2) Å and 84.39 (7)° for (II). Each Cu atom is five-coordinated and the coordination geometry around the Cu atom is best described as a distorted square-pyramid with a $\tau$ value of 0.155 (3) for (I) and 0.092 (7) for (II). The apical Cu—Cl bond length is 2.852 (1) Å for (I) and 2.971 (2) Å for (II). The basal Cu—Cl and Cu—N average bonds lengths are 2.2673 (9) and 2.030 (2) Å, respectively, for (I), and 2.280 (2) and 2.038 (6) Å for (II). The molecules of (I) are linked by one C—H$\cdots$Cl hydrogen bond into a complex [10$\bar{1}$] sheet. The molecules of (II) are linked by one C—H$\cdots$Cl and one N—H$\cdots$O hydrogen bond into a complex [100] sheet.

## Comment

Dinuclear transition metal complexes have received much attention because of their relevance as models for active sites of biomolecules, such as hemocyanin, tyrosinase and copper oxidases (Pradeep *et al.*, 2005; Sorrell, 1989), and also because of the correlation between their structure and magnetic behaviour (Schuitema *et al.*, 2002; Rodríguez *et al.*, 2000). Among these dinuclear transition metal complexes, some anions, such as OH$^-$, *R*O$^-$, *R*CO$_2^-$, Cl$^-$ and Br$^-$, are often used as bridging ligands (Christou *et al.*, 2000). Many dichloride-bridged dinuclear copper systems have been reported in the literature and different magnetic behaviours observed (Rodríguez *et al.*, 2000; Schuitema *et al.*, 2002; Tuna *et al.*, 1999), and the magneto-structural correlation, which relates the magnetic interaction to $\varphi/R$ (as defined below), has been established (Marsh *et al.*, 1982). Copper complexes containing diimines have also been extensively studied and reported owing to their potential applications (Alvesa *et al.*, 2004). Previously, our group has reported the structures of some transition metal complexes with diimines (Han *et al.*, 2006; Liu *et al.*, 2007; Xia *et al.*, 2007; Yang *et al.*, 2007). For this reason, we have synthesized two new dichloride-bridged dinuclear copper complexes with diimines, di-$\mu$-chlorido-



(I)



(II)

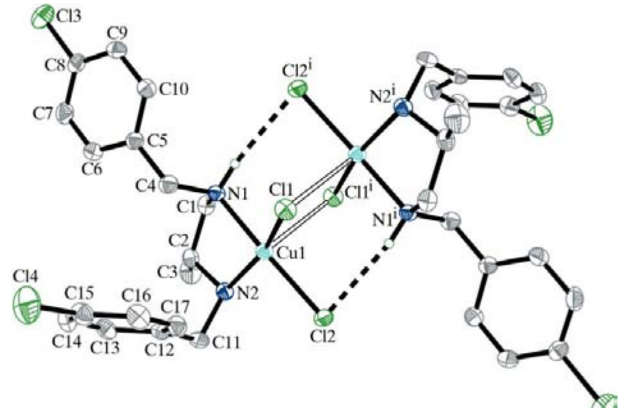


**Figure 1**
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, H atoms have been omitted. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

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bis{[$N$,$N'$-bis(4-chlorobenzyl)propane-1,2-diamine]chloridocopper(II)}, (I), and di-$\mu$-chlorido-bis{[$N$,$N'$-bis(3,4-methylenedioxybenzyl)propane-1,2-diamine]chloridocopper(II)}, (II), whose syntheses and structures are reported here.

Complexes (I) and (II) have similar coordination environments (Figs. 1 and 2). In each complex, the asymmetric unit consists of one half-molecule; two copper centres are bridged by a pair of Cl atoms, resulting in a complex with a centrosymmetric structure containing a Cu($\mu$-Cl)$_2$Cu parallelogram core. The Cu$\cdots$Cu separation of 3.4285 (8) Å for (I) is smaller than those values reported in two dichloride-bridged dinuclear copper(II) complexes, *viz.* [Cu$_2$(5-aminomethyl-3-methylpyrazole)$_2$Cl$_4$], (III) [Cu$\cdots$Cu = 3.479 (4) Å; Schuitema *et al.*, 2002], and {[Cu$L_2$Cl$_2$]$_2$[ClO$_4$]$_2$}, (IV) [where $L$ is 1-(imidazol-4-ylmethyl)-l,5-diazacyclooctane; Cu$\cdots$Cu = 3.494 (8) Å; Bu *et al.*, 2001], in which magnetic coupling between the copper centres can be observed; however, the Cu$\cdots$Cu separation of 3.565 (2) Å for (II) is longer than those of (III) and (IV). The Cu—Cl—Cu angles are 83.36 (3)° for (I) and 84.39 (7)° for (II); these values are smaller than those of (III) and (IV), in which the Cu—Cl—Cu angles range from 85.33 (15) to 88.81 (5)°. Each Cu atom in (I) and (II) is five-coordinated by two N atoms of one ligand and three Cl atoms, and the coordination polyhedron around the Cu atom may be described as a slightly distorted square pyramid with $\tau$ values (Addison *et al.*, 1984) of 0.155 (3) for (I) and 0.092 (7) for (II), where $\tau$ is defined as $(\beta - \alpha)/60$, and $\beta$ and $\alpha$ are the largest coordination angles ($\tau$ = 0 for a regular square-pyramidal geometry and $\tau$ = 1 for trigonal-bipyramidal geometry). The apical position is occupied by one elongated bridging Cl atom, and the apical Cu—Cl bond distances are 2.852 (1) Å for (I) and 2.971 (2) Å for (II); these values are longer than those of (III) and (IV), in which the apical Cu—Cl bond distances range from 2.6571 (14) to 2.829 (4) Å. The basal planes are defined by atoms Cl1, Cl2, N1 and N2; atoms Cu1 are shifted by 0.106 (1) Å for (I) and 0.050 (3) Å for (II) from the basal planes toward the apical Cl1$A$ atom. The basal Cu—Cl and Cu—N average bond lengths are 2.2673 (9) and 2.030 (2) Å in (I), and 2.280 (2) and 2.038 (6) Å in (II) (see in Tables 1 and 3).

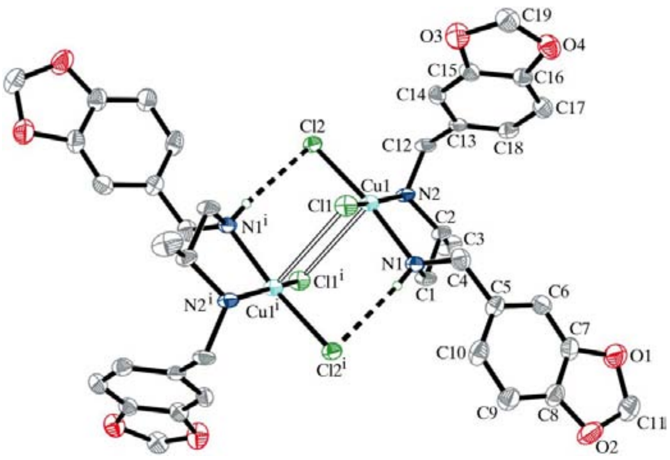

**Figure 2**
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, H atoms have been omitted. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

Generally, dichloride-bridged dinuclear copper complexes with square-pyramidal geometry exhibit three different geometries with regard to the relative arrangement of square pyramids, *viz.* perpendicular bases (type I), parallel bases

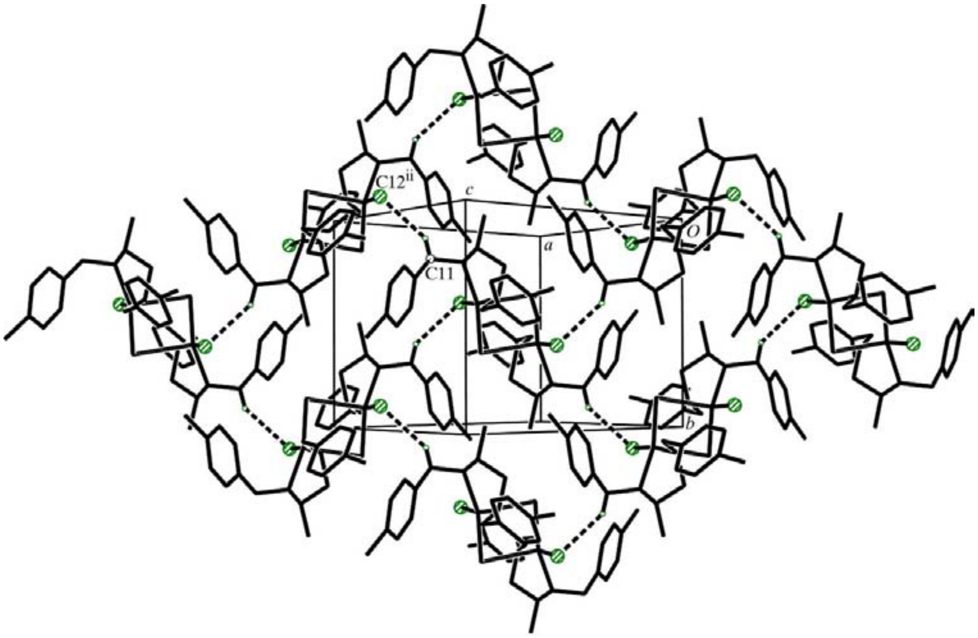

**Figure 3**
Part of the crystal structure of (I), showing the formation of a [10$\overline{1}$] sheet. For clarity, H atoms have been omitted. Dashed lines indicate hydrogen bonds. [Symmetry code: (ii) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$.]

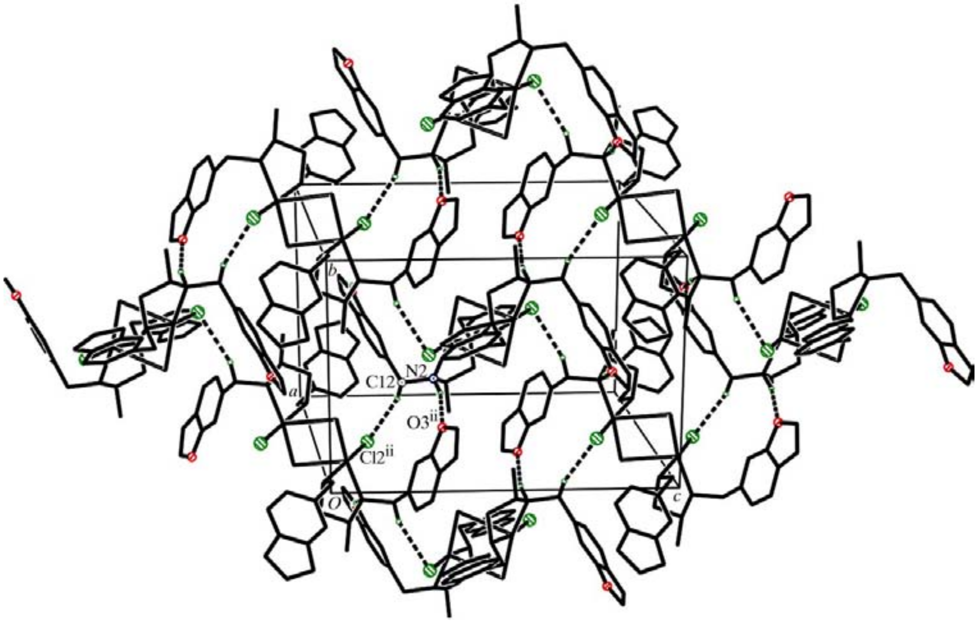

**Figure 4**
Part of the crystal structure of (II), showing the formation of a [100] sheet. For clarity, H atoms have been omitted. Dashed lines indicate hydrogen bonds. [Symmetry code: (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.]

(type II) and coplanar bases (type III) (Rodríguez *et al.*, 2000). In the parallel bases case, two square pyramids share a base-to-apex edge, so that a Cl atom situated at the vertex of one base becomes the apical vertex of the other square pyramid. The symmetric arrangements of the Cu($\mu$-Cl)$_2$Cu cores in complexes (I) and (II) belong to type II. The two intramolecular basal planes are strictly parallel, with interplanar spacings of 2.731 (6) Å for (I) and 2.82 (3) Å for (II), corresponding to plane offsets of 2.07 (1) Å for (I) and 2.18 (4) Å for (II); the dihedral angles between the Cu($\mu$-Cl)$_2$Cu parallelogram core and the basal plane are 87.27 (4)° for (I) and 86.85 (8)° for (II).

Some theoretical analysis and experiments concerning the magneto-structural correlation for dichloride-bridged dinuclear copper(II) complexes can be found in the literature (Schuitema *et al.*, 2002; Rodríguez *et al.*, 2000; Tuna *et al.*, 1999). Marsh *et al.* (1982) have shown that the exchange coupling interaction depends on the magnitude of the angle at the Cu—Cl—Cu bridge, $\varphi$, as well as the apical Cu—Cl bond length, $R$. It was found that, for values of the quotient $\varphi/R$ that are lower than 32.6° Å$^{-1}$ and higher than 34.88° Å$^{-1}$, the exchange interaction is antiferromagnetic. For values falling between these limits, the exchange interaction was found to be ferromagnetic. In the cases of (I) and (II), the values of the quotient $\varphi/R$ are 29.23 (2) and 28.40 (4)° Å$^{-1}$, respectively; both quotients are below the border value of 32.6° Å$^{-1}$, suggesting an antiferromagnetic interaction between the two copper(II) ions.

In the crystal structures of (I) and (II), the molecules are stabilized by a pair of intramolecular N—H$\cdots$Cl hydrogen bonds (Figs. 1 and 2, and Tables 2 and 4). In (I), the molecules are linked by a single intermolecular C—H$\cdots$Cl hydrogen bond; atom C11 at ($x, y, z$) in the molecule centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) acts as a hydrogen-bond donor, *via* H11*B*, to atom Cl2 at ($-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$) in the molecule centred at (1, 0, 1), and propagation is *via* inversion, the screw axis and translation generating a complex sheet in [$10\overline{1}$] (Fig. 3 and Table 2).

In (II), the molecules are linked by one intermolecular C—H$\cdots$Cl and one N—H$\cdots$O hydrogen bond; atoms C12 and N2 at ($x, y, z$) in the molecule centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) act as hydrogen-bond donors, *via* H12*A* and H2, to atoms Cl2 and O3 at ($-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$) in the molecule centred at (1, 0, 1), and propagation *via* a screw axis and translation generates a complex sheet in [100] (Fig. 4 and Table 4).

## Experimental

For the preparation of complex (I), a solution of copper chloride (0.48 g, 3 mmol) in ethanol (10 ml) was added dropwise with stirring to a solution of *N*,*N*-bis(4-chlorobenzyl)propane-1,2-diamine (0.96 g, 3 mmol) in ethanol (20 ml). The reaction mixture was stirred for 3 h at 333–343 K and then left to cool at room temperature; the solid obtained was filtered off, washed successively with chloroform (3 × 3 ml) and ethanol (3 × 3 ml), and dried at room temperature. Green crystals of (I) suitable for X-ray structure analysis were obtained by slow evaporation of a dimethylformamide–ethanol (1:10) solution containing the product over a period of three weeks (yield 0.98 g, 68%; m.p. 466–469 K). Analysis calculated for $C_{34}H_{40}Cl_8Cu_2N_4$: C 44.61, H 4.40, N 6.12%; found: C 45.22, H 4.28, N 5.88%. IR (KBr, cm$^{-1}$): 3450, 3162, 2946, 1599, 1551, 1492, 1440, 1089, 1013, 922, 810, 704, 566.

Using the same method, green crystals of complex (II) suitable for X-ray structure analysis were also obtained (yield 1.18 g, 71%; m.p. 509–512 K). Analysis calculated for $C_{38}H_{44}Cl_4Cu_2N_4O_8$: C 47.86, H 4.65, N 5.87%; found: C 48.48, H 4.49, N 6.02%. IR (KBr disk, cm$^{-1}$): 3464, 3250, 2932, 1599, 1553, 1493,1447, 1252, 1034, 922, 812, 767, 704.

## Compound (I)

*Crystal data*

$[Cu_2Cl_4(C_{17}H_{20}Cl_2N_2)_2]$
$M_r$ = 915.38
Monoclinic, $P2_1/n$
$a$ = 14.4217 (15) Å
$b$ = 9.5445 (13) Å
$c$ = 15.6198 (19) Å
$\beta$ = 115.647 (2)°
$V$ = 1938.2 (4) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.68 mm$^{-1}$
$T$ = 298 (2) K
0.54 × 0.50 × 0.46 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.464, $T_{max}$ = 0.512 (expected range = 0.418–0.462)
8896 measured reflections
3417 independent reflections
2484 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.038

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.082
$S$ = 1.06
3417 reflections
218 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.28 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu1—N1 | 2.026 (2) | Cu1—Cl2 | 2.2742 (9) |
| Cu1—N2 | 2.033 (2) | Cu1—Cl1$^{i}$ | 2.852 (1) |
| Cu1—Cl1 | 2.2604 (9) | Cu1—Cu1$^{i}$ | 3.4285 (8) |
| | | | |
| N1—Cu1—N2 | 83.69 (9) | Cl1—Cu1—Cl2 | 96.18 (3) |
| N1—Cu1—Cl1 | 92.41 (7) | N1—Cu1—Cl1$^{i}$ | 82.32 (7) |
| N2—Cu1—Cl1 | 159.84 (8) | N2—Cu1—Cl1$^{i}$ | 102.40 (7) |
| N1—Cu1—Cl2 | 169.01 (7) | Cl1—Cu1—Cl1$^{i}$ | 96.64 (3) |
| N2—Cu1—Cl2 | 90.49 (7) | Cl2—Cu1—Cl1$^{i}$ | 89.87 (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···$A$ |
|---|---|---|---|---|
| N1—H1···Cl2$^{i}$ | 0.91 | 2.57 | 3.450 (3) | 164 |
| C11—H11$B$···Cl2$^{ii}$ | 0.97 | 2.82 | 3.659 (3) | 145 |
| C13—H13···Cl3$^{iii}$ | 0.93 | 2.89 | 3.810 (3) | 170 |

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

## Compound (II)

*Crystal data*

$[Cu_2Cl_4(C_{19}H_{22}N_2O_4)_2]$
$M_r$ = 953.65
Monoclinic, $P2_1/c$
$a$ = 12.2965 (13) Å
$b$ = 11.0554 (12) Å
$c$ = 15.822 (2) Å
$\beta$ = 98.140 (2)°
$V$ = 2129.2 (4) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.30 mm$^{-1}$
$T$ = 298 (2) K
0.45 × 0.37 × 0.31 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.592, $T_{max}$ = 0.688
10028 measured reflections
3730 independent reflections
2008 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.162

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.217
$S$ = 1.14
3730 reflections
254 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.12 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.64 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu1—N1 | 2.032 (6) | Cu1—Cl1 | 2.282 (2) |
| Cu1—N2 | 2.044 (6) | Cu1—Cl1$^{i}$ | 2.971 (2) |
| Cu1—Cl2 | 2.278 (2) | Cu1—Cu1$^{i}$ | 3.565 (2) |
| | | | |
| N1—Cu1—N2 | 84.5 (2) | N1—Cu1—Cl1$^{i}$ | 81.5 (2) |
| N1—Cu1—Cl2 | 170.0 (2) | N2—Cu1—Cl1$^{i}$ | 98.3 (2) |
| N2—Cu1—Cl2 | 92.1 (2) | Cl2—Cu1—Cl1$^{i}$ | 89.70 (7) |
| N1—Cu1—Cl1 | 90.4 (2) | Cl1—Cu1—Cl1$^{i}$ | 95.61 (7) |
| N2—Cu1—Cl1 | 164.3 (2) | Cu1—Cl1—Cu1$^{i}$ | 84.39 (7) |
| Cl2—Cu1—Cl1 | 95.26 (8) | | |

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···$A$ |
|---|---|---|---|---|
| N1—H1···Cl2$^{i}$ | 0.91 | 2.58 | 3.476 (6) | 169 |
| N2—H2···O3$^{ii}$ | 0.91 | 2.20 | 3.075 (9) | 160 |
| C12—H12$A$···Cl2$^{ii}$ | 0.97 | 2.84 | 3.774 (8) | 162 |
| C11—H11$A$···Cl1$^{iii}$ | 0.97 | 2.87 | 3.779 (11) | 156 |

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

All H atoms were located in difference Fourier maps and treated as riding atoms, with C—H distances of 0.98 (methine), 0.93 (aryl), 0.96 (methyl) and 0.97 Å (methylene), N—H distances of 0.91 Å, and $U_{iso}$(H) values of 1.2$U_{eq}$(methine, aryl and methylene C, and imine N) and 1.5$U_{eq}$(methyl C). The value of $R_{int}$ for complex (II) is high because of the poor crystal quality, resulting in broad diffraction peaks.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3060). Services for accessing these data are described at the back of the journal.

## References

Addison, A. W., Rao, T. N., Reedijk, J., Rijn, J. V. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Alvesa, W. A., de Almeida-Filhoa, S. A., de Almeida Santosb, R. H., Paduan-Filhoc, A. & da Costa Ferreira, A. M. (2004). *J. Braz. Chem. Soc.* **15**, 872–883.

Bu, X.-H., Du, M., Zhang, L., Shang, Z.-L., Ruo-Hua Zhang, R.-H. & Shionoya, M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 729–735.

Christou, G., Gatteschi, D. N., Hendrickson, D. N. & Sessoli, R. (2000). *MRS Bull.* **25**, 66–71.

Han, L.-J., Yang, S.-P., Wang, D.-Q. & Xia, H.-T. (2006). *Acta Cryst.* E**62**, m2607–m2609.

Liu, Y.-F., Xia, H.-T., Yang, S.-P. & Wang, D.-Q. (2007). *Acta Cryst.* E**63**, m332–m334.

Marsh, W. E., Hatfield, W. E. & Hodgson, D. J. (1982). *Inorg. Chem.* **21**, 2679–2684.

Pradeep, C. P., Zacharias, P. S. & Das, S. K. (2005). *J. Chem. Sci.* **117**, 133–137.

Rodríguez, M., Llobet, A. & Corbella, M. (2000). *Polyhedron*, **19**, 2483–2491.

Schuitema, A. M., Stassen, A. F., Driessen, W. L. & Reedijk, J. (2002). *Inorg. Chim. Acta*, **337**, 48–52.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sorrell, T. N. (1989). *Tetrahedron*, **45**, 3–68.

Tuna, F., Patron, L., Journaux, Y., Andruh, M., Plass, W. & Trombee, J.-C. (1999). *J. Chem. Soc. Dalton Trans.* pp. 539–545.

Xia, H.-T., Liu, Y.-F., Wang, D.-Q. & Yang, S.-P. (2007). *Acta Cryst.* E**63**, m1162–m1164.

Yang, S.-P., Han, L.-J., Wang, D.-Q. & Xia, H.-T. (2007). *Acta Cryst.* E**63**, m2763.