

# Crystal structure of a mixed-ligand silver(I) complex of the non-steroidal anti-inflammatory drug diclofenac and pyrimidine

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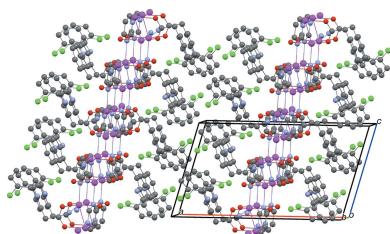
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In the title mixed-ligand silver(I) coordination polymeric complex with the non-steroidal anti-inflammatory drug diclofenac ( $C_{14}H_{11}Cl_2NO_2$ ) (diclH) and pyrimidine (pym), namely poly $[\{\mu_2$ -2-[2-(2,6-dichloroanilino)phenyl]acetato- $\kappa^2O:O'\}(\mu_2$ -pyrimidine- $\kappa^2N^1:N^3$ )silver(I)],  $[Ag(C_{14}H_{10}Cl_2NO_2)(C_4H_4N_2)]_n$  or  $[Ag(\mu$ -dicl)( $\mu$ -pym)] $_n$ , the very distorted tetrahedral  $AgN_2O_2$  coordination centres comprise two N-atom donors from bridging pym ligands [ $Ag-N = 2.381(3)$  and  $2.412(3)$  Å] and two carboxylate O-atom donors from dicl ligands [ $Ag-O = 2.279(2)$  and  $2.280(2)$  Å], which bridge Ag atoms, giving a centrosymmetric dinuclear units with a short  $Ag \cdots Ag$  separation [ $2.8931(5)$  Å]. Within the units are short intraligand  $C-Cl \cdots \pi$ (pym) interactions [ $3.6409(15)$  Å]. The units are linked through the bridging N atoms of the pym ligand into a two-dimensional sheet-polymer structure lying parallel to (100) and stabilized by inter-ring  $\pi$ - $\pi$  interactions between the pym ligands [ $Cg \cdots Cg = 3.4199(17)$  Å]. Additional inter-unit  $C-H \cdots O$  and  $C-H \cdots Cg$  hydrogen-bonding interactions between the sheets give an overall three-dimensional structure.

## 1. Chemical context

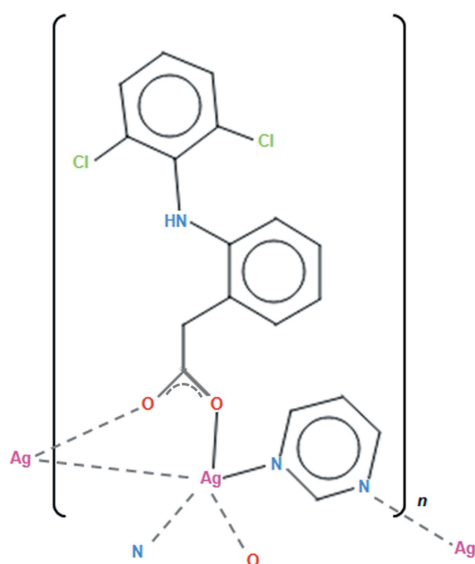
The design of coordination polymers based on silver(I) has been studied extensively in recent years because of their various structural topologies as well as photoluminescent properties and antimicrobial activity. These studies have shown that short  $Ag \cdots Ag$  separations are one of the most important factors for the manifestation of such properties [Yam & Lo, 1999; Pyykkö *et al.*, 1997; Wang & Cohen, 2009; Zhang *et al.*, 2009; Njogu *et al.*, 2015; Nomiya *et al.*, 2000]. On the other hand, it is known that to construct extended coordination networks with polynuclear metal-based structures, ligands of various binding sites and shapes have to be taken into account. At this stage, confidence in accomplishing this goal is based upon the sophisticated selection and utilization of suitable multifunctional organic ligands with certain features, such as being a multiple donor and having versatile bonding modes or the ability to take part in hydrogen bonding. Aromatic carboxylate derivatives have therefore been of interest in coordination and supramolecular chemistry.

The chemical classes of non-steroidal anti-inflammatory drugs (NSAIDs) consist of salicylate derivatives, phenylalkanoic acids, oxicams, anthranilic acids, sulfonamides and furanones (Weder *et al.*, 2002). These compounds are some of the most commonly used medications to reduce pain, and



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diclofenac (dicl), [2-(2,6-dichloroanilino)phenylacetic acid], is a member of the group of phenylalkanoic acids. Additionally, NSAIDs are used as anti-inflammatories, antipyretics and antitumor drugs. (Kim *et al.*, 2004; Ribeiro *et al.*, 2008; Duffy *et al.*, 1998). In previous publications, the crystal structures of metal complexes of diclofenac have been reported (Caglar *et al.*, 2013, 2014; Ali & Jabali, 2016; Dimiza *et al.*, 2011; Kovalad-Demertzi *et al.*, 1997; Castellari *et al.*, 1999; Kourkoumelis *et al.*, 2004) and in addition its molecular structure has been characterized by various techniques (Iliescu *et al.*, 2004). Based on the above-mentioned points, we report herein the synthesis and structural characterization of a new mixed-ligand silver(I) complex with dicl and pyrimidine (pym), namely  $[\text{Ag}(\mu\text{-dicl})(\mu\text{-pym})]_n$ , (I).



## 2. Structural commentary

In (I), Ag1 atoms are four-coordinated by two carboxylate oxygen atoms [O2 and O1<sup>i</sup>; symmetry code: (i)  $-x + 1, -y + 1$ ,

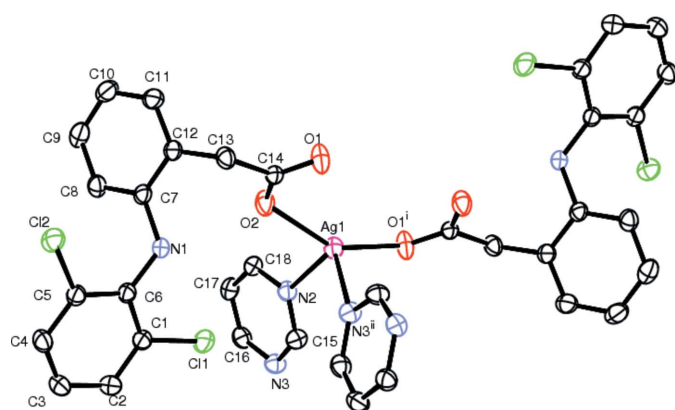


Figure 1

The molecular configuration and atom-labelling scheme for the title complex, (I), with displacement ellipsoids drawn at the 30% level. For symmetry codes (i) and (ii), see Table 1.

Table 1

Selected geometric parameters (Å, °).

Ag1—O2	2.279 (2)	Ag1—N3 <sup>ii</sup>	2.412 (3)
Ag1—O1 <sup>i</sup>	2.280 (2)	Ag1—Ag1 <sup>i</sup>	2.8931 (5)
Ag1—N2	2.381 (3)		
O2—Ag1—O1 <sup>i</sup>	148.04 (10)	O2—Ag1—Ag1 <sup>i</sup>	81.70 (6)
O2—Ag1—N2	99.71 (8)	O1 <sup>i</sup> —Ag1—Ag1 <sup>i</sup>	76.19 (6)
O1 <sup>i</sup> —Ag1—N2	89.58 (8)	N2—Ag1—Ag1 <sup>i</sup>	151.80 (6)
O1 <sup>i</sup> —Ag1—N3 <sup>ii</sup>	108.69 (9)	N3 <sup>ii</sup> —Ag1—Ag1 <sup>i</sup>	99.73 (6)
N2—Ag1—N3 <sup>ii</sup>	107.93 (9)		

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

$-z + 2$ ] from separate dicl ligands and two nitrogen atoms [N2 and N3<sup>ii</sup>; symmetry code: (ii)  $x, -y + \frac{1}{2}, -z + \frac{1}{2}$ ] from two separate pym ligands (Fig. 1). The discrimination parameter for the  $\text{AgN}_2\text{O}_2$  core  $\{\tau_4 = [(360^\circ - (\alpha + \beta))/141^\circ]$ , where  $\alpha$  and  $\beta$  are the largest angles around the metal atom) is 0.732 and indicates substantial deviation from ideal tetrahedral geometry (Yang *et al.*, 2007). The Ag—N bond lengths [2.381 (3) and 2.412 (3) Å] (Table 1) are similar to those found in the polymeric mixed-ligand silver(I) complex with 3,5-pyridinedicarboxylate (pydc) and (pym),  $[\text{Ag}_4(\mu\text{-pydc})_2(\mu\text{-pym})_2]_n$  [2.313 (5), 2.436 (5) and 2.490 (5) Å; Hamamci Alisir *et al.*, 2015). The Ag—O bond lengths in (I) [2.279 (2) and 2.280 (2) Å] are longer than those in  $[\text{Ag}_2(\text{sal})_2]_n$  (sal = salicylate; 2.1887–2.2043 Å; Azócar *et al.*, 2013) but shorter than those found in other silver carboxylate complexes (Wu & Mak, 1995; Zhang *et al.*, 2015; Olson *et al.*, 2006). Each pair of silver(I) atoms in the title complex is bridged by the  $\mu_2$ -carboxylato-*O,O'* groups of dicl, forming centrosymmetric

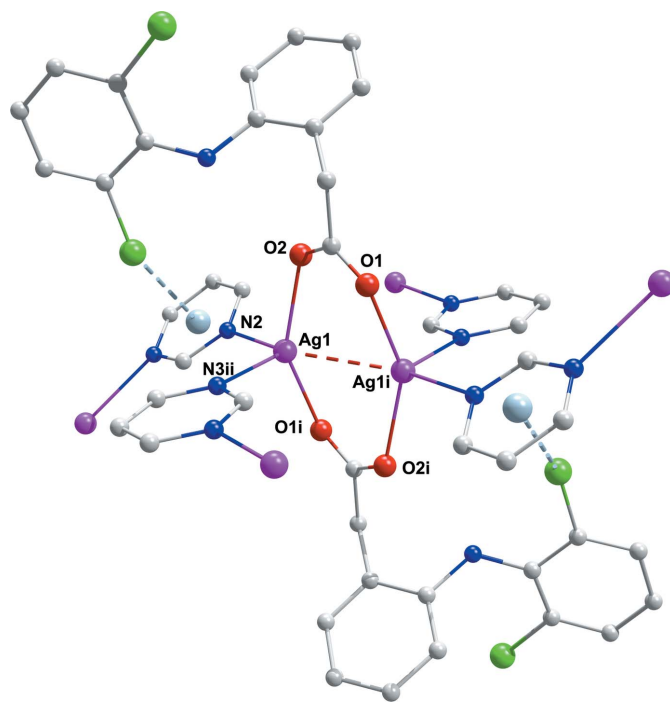


Figure 2

A view of the centrosymmetric carboxylate-bridged dinuclear  $[\text{Ag}_2(\mu\text{-dicl})_2]$  unit in (I). H atoms have been omitted.

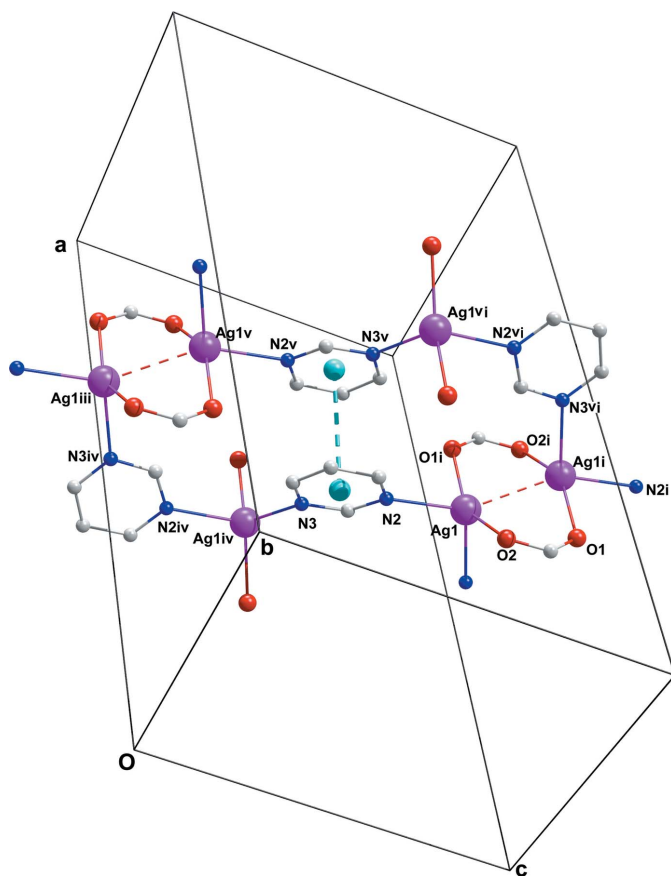
**Table 2**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots O2$	0.86	2.43	2.971 (3)	122
$C16-H16\cdots O1^{iii}$	0.93	2.51	3.248 (4)	136
$C13-H13B\cdots Cg6^{iv}$	0.97	3.30	3.983 (3)	129

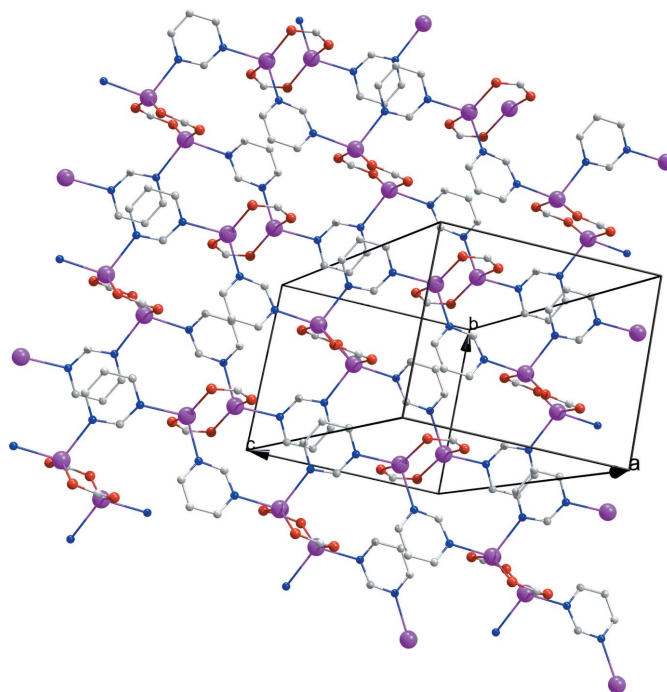
Symmetry codes: (iii)  $x, y, z - 1$ ; (iv)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ .

dinuclear  $[Ag_2(\mu\text{-dicl})_2]$  units (Fig. 2). Within the units are short intraligand  $C1-C11\cdots\pi$  interactions to the pym ligands [3.6409 (15) Å]. The  $Ag1\cdots Ag1^i$  separation in the unit [2.8931 (5) Å] is significantly shorter than the sum of the van der Waals radii for two silver atoms (3.44 Å), indicating weak interactions between adjacent  $Ag^I$  ions, forming an  $[Ag_2(COO)_2]$  units. If coexisting strong argentophilic  $Ag1\cdots Ag1^i$  interactions are considered as coordinative, it could be reasoned that the coordination around  $Ag1$  is slightly distorted trigonal-bipyramidal [the structural distortion index  $\tau$  ( $\tau$ ) was calculated to be 0.06] (Addison *et al.*, 1984).

As illustrated in Fig. 3, in the title complex, the pym ligand acts as a  $\mu_2-N, N'$ -bridging ligand between neighboring  $[Ag_2(COO)_2]$  units, leading to the formation of a two-dimensional coordination polymer, extending along (100) (Fig. 4). In other words,  $[Ag_2(COO)_2]$  units, which comprise



**Figure 3**  
A partial expansion of the dinuclear unit in (I) through the pym ligands, also showing the  $pym\cdots pym$   $\pi$ - $\pi$  ring interactions.



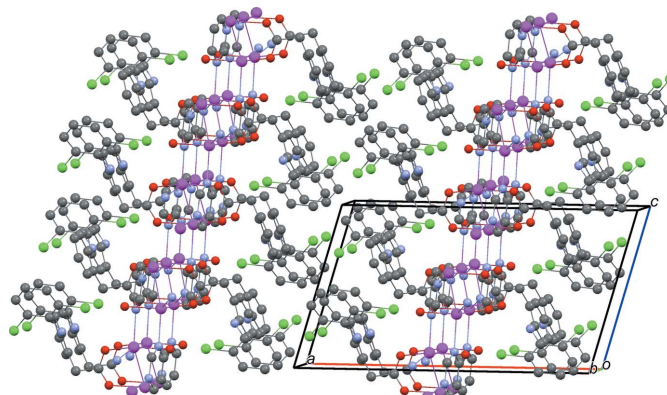
**Figure 4**  
The layered structure of (I). H atoms and part of the dicl ligands have been omitted.

eight-membered rings, can be defined as the nodes of the structure. Connection of the four different pym ligands to these nodes provides continuity of the structure (Fig. 4).

In the dicl ligand, the two benzene rings form a dihedral angle of  $61.42 (5)^\circ$ , the conformation of the ligand being stabilized by an intramolecular  $N1-H1\cdots O2_{\text{carboxyl}}$  hydrogen-bonding interaction [2.971 (3) Å] (Table 2).

### 3. Supramolecular features

In the crystal, a  $C16-H16\cdots O1^{iii}$  hydrogen-bonding interaction stabilizes the crystal packing (Table 2). In addition, there is a weak  $C13-H13\cdots Cg6^{iv}$  interaction to a pym ring [3.983 Å] and a strong  $\pi$ - $\pi$  stacking interaction between



**Figure 5**  
The packing of (I) in the unit cell viewed along the  $b$  axis.

Table 3

Selected comparative IR spectral data for Nadicl and the diel ligand in (I).

Frequencies in  $\text{cm}^{-1}$ ; w, weak; m, medium; s, strong; vs, very strong. Nadicl = sodium 2-(2,6-dichloroanilino)phenylacetate.

Assignment	Nadicl	(I)
$\nu(\text{NH})$	3250 (m)	3307 (m)
$\nu_{\text{ar}}(\text{CH})$	3060 (vw)	3064–3029 (vw)
$\nu_{\text{al}}(\text{CH})$	2980 (vw)	2956–2890 (vw)
$\nu_{\text{as}}(\text{COO})$	1572 (vs)	1548 (vs)
$\nu_{\text{s}}(\text{COO})$	1399 (w)	1365 (vs)
$\nu(\text{CCL})$	768 (s)	768 (vs)

aromatic rings of the pym ligands [ $\text{Cg3} \cdots \text{Cg3}^{\text{v}} = 3.4199$  (17) Å;  $\text{Cg3}$  is the centroid of the  $\text{N2/C15/N3/C216-C18}$  ring; symmetry code (v):  $-x + 1, -y + 1, -z + 1$ ], shown in Fig. 3. These interactions are significant for holding layers together in the solid state and generating an overall three-dimensional framework structure (Fig. 5).

#### 4. Synthesis and crystallization

All reactions were performed with commercially available reagents and used without further purification. Solid sodium 2-(2,6-dichloroanilino)phenylacetate (Nadicl) (0.32 g, 1 mmol) and pyrimidine (0.08 g, 1 mol) were added to an aqueous solution (10  $\text{cm}^3$ ) of  $\text{AgNO}_3$  (0.17 g, 1 mmol) with stirring. A white suspension with a white precipitate formed and the addition of acetonitrile (10  $\text{cm}^3$ ) to this resulted in a clear solution which was left to stand for slow evaporation in darkness at room temperature. Single crystals of (I) suitable for X-ray analysis were obtained within a few days.

#### 5. Spectroscopy

The infrared spectrum was obtained using a Perkin Elmer Spectrum Two FTIR with a diamond Attenuated Total Reflectance attachment (ATR) in the frequency range 4000–600  $\text{cm}^{-1}$ . The sample was placed on the ATR crystal and pressure exerted by screwing the pressure clamp onto the sample to ensure maximum contact with the ATR crystal. The characteristic absorption bands of Nadicl and the title complex are listed in Table 3. The spectrum is deposited as a supplementary Fig. S1.

The characteristic absorption band in the FT-IR spectra of the carboxylate complexes is the asymmetric ( $\nu_{\text{as}}$ ) and symmetric ( $\nu_{\text{s}}$ ) vibrations of the carboxylate group. The difference between the asymmetric and symmetric carboxylate stretching [ $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ ] is often used to correlate the infrared spectra of metal carboxylate structures. When  $\Delta\nu < 200 \text{ cm}^{-1}$ , the carboxylate groups of the complexes can be considered bidentate (Azócar *et al.*, 2013). The value of  $\Delta\nu$  is calculated as 183  $\text{cm}^{-1}$  for 1. Based on the above-mentioned points, it is suggested that carboxylate groups in the complex exhibit a bidentate coordination mode, as revealed by the structural analysis.

Table 4

Experimental details.

Crystal data	
Chemical formula	$[\text{Ag}(\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NO}_2)(\text{C}_4\text{H}_4\text{N}_2)]$
$M_r$	483.09
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
$a, b, c$ (Å)	18.5886 (4), 9.3071 (4), 10.6646 (8)
$\beta$ (°)	105.644 (3)
$V$ (Å <sup>3</sup> )	1776.69 (16)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.45
Crystal size (mm)	0.60 × 0.46 × 0.27
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Integration ( $X\text{-RED}32$ ; Stoe & Cie, 2002)
$T_{\text{min}}, T_{\text{max}}$	0.471, 0.693
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	13090, 4538, 3672
$R_{\text{int}}$	0.088
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.675
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.095, 1.04
No. of reflections	4538
No. of parameters	236
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.57, -1.14

Computer programs:  $X\text{-AREA}$  and  $X\text{-RED}32$  (Stoe & Cie, 2002),  $SHELXS97$  (Sheldrick, 2008) within  $WinGX$  (Farrugia, 2012),  $SHELXL2014$  (Sheldrick, 2015),  $ORTEP-3$  for Windows (Farrugia, 2012) and  $SHELXTL$  (Sheldrick, 2008).

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All C-bound hydrogen atoms in (I) were included in calculated positions with  $\text{C-H} = 0.93$  Å (aromatic) or  $0.97$  Å (methylene) and allowed to ride, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The N-bound H atom was located in a difference-Fourier map but was also allowed to ride in the refinement with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ .

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## supporting information

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## Crystal structure of a mixed-ligand silver(I) complex of the non-steroidal anti-inflammatory drug diclofenac and pyrimidine

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### Computing details

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-Area* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Poly[{ $\mu_2$ -2-[2-(2,6-dichloroanilino)phenyl]acetato- $\kappa^2 O:O'$ }( $\mu_2$ -pyrimidine- $\kappa^1 N^1:N^3$ )silver(I)]

### Crystal data

[Ag(C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>NO<sub>2</sub>)(C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>)]

$M_r = 483.09$

Monoclinic,  $P2_1/c$

$a = 18.5886$  (4) Å

$b = 9.3071$  (4) Å

$c = 10.6646$  (8) Å

$\beta = 105.644$  (3)°

$V = 1776.69$  (16) Å<sup>3</sup>

$Z = 4$

$F(000) = 960$

$D_x = 1.806$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 13681 reflections

$\theta = 2.0\text{--}29.1^\circ$

$\mu = 1.45$  mm<sup>-1</sup>

$T = 293$  K

Prism, colorless

$0.60 \times 0.46 \times 0.27$  mm

### Data collection

Stoe IPDS2

diffractometer

$\omega$ -scan rotation method

Absorption correction: integration

(X-RED32; Stoe & Cie, 2002)

$T_{\min} = 0.471$ ,  $T_{\max} = 0.693$

13090 measured reflections

4538 independent reflections

3672 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.088$

$\theta_{\max} = 28.7^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -24 \rightarrow 24$

$k = -12 \rightarrow 12$

$l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.095$

$S = 1.04$

4538 reflections

236 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.57$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.14$  e Å<sup>-3</sup>

Extinction correction: SHELXL2014

(Sheldrick, 2015),

$F_c^* = kFc[1 + 0.001x(Fc^2\lambda^3/\sin(2\theta))]^{-1/4}$

Extinction coefficient: 0.0206 (11)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.17222 (14)	0.3200 (3)	0.6246 (3)	0.0419 (6)
C2	0.12206 (16)	0.2364 (3)	0.5353 (3)	0.0496 (7)
H2	0.1387	0.1695	0.4847	0.060*
C3	0.04629 (16)	0.2541 (4)	0.5223 (4)	0.0546 (8)
H3	0.0116	0.2009	0.4607	0.065*
C4	0.02263 (15)	0.3495 (4)	0.5995 (3)	0.0505 (7)
H4	−0.0282	0.3603	0.5912	0.061*
C5	0.07381 (14)	0.4302 (3)	0.6904 (3)	0.0406 (6)
C6	0.15110 (13)	0.4220 (3)	0.7029 (3)	0.0381 (5)
C7	0.19762 (12)	0.6542 (3)	0.8068 (3)	0.0377 (5)
C8	0.15520 (14)	0.7377 (3)	0.7067 (3)	0.0451 (6)
H8	0.1312	0.6953	0.6275	0.054*
C9	0.14820 (16)	0.8839 (4)	0.7235 (4)	0.0529 (8)
H9	0.1197	0.9397	0.6558	0.063*
C10	0.18355 (17)	0.9463 (3)	0.8408 (4)	0.0573 (9)
H10	0.1785	1.0443	0.8535	0.069*
C11	0.22657 (15)	0.8624 (3)	0.9396 (4)	0.0501 (7)
H11	0.2502	0.9054	1.0187	0.060*
C12	0.23575 (12)	0.7165 (3)	0.9249 (3)	0.0391 (6)
C13	0.28437 (13)	0.6294 (4)	1.0340 (3)	0.0437 (6)
H13A	0.2575	0.5429	1.0448	0.052*
H13B	0.2930	0.6843	1.1140	0.052*
C14	0.36042 (13)	0.5857 (3)	1.0147 (3)	0.0367 (5)
C15	0.44153 (16)	0.3069 (3)	0.5812 (3)	0.0444 (6)
H15	0.4577	0.2251	0.6310	0.053*
C16	0.40626 (15)	0.4123 (3)	0.3828 (3)	0.0461 (6)
H16	0.3968	0.4080	0.2926	0.055*
C17	0.39630 (16)	0.5399 (4)	0.4394 (3)	0.0489 (7)
H17	0.3807	0.6220	0.3899	0.059*
C18	0.41040 (15)	0.5417 (3)	0.5740 (3)	0.0461 (6)
H18	0.4038	0.6266	0.6154	0.055*
Ag1	0.46373 (2)	0.43353 (3)	0.87652 (2)	0.04354 (10)
Cl1	0.26694 (4)	0.29612 (9)	0.63922 (10)	0.0610 (2)
Cl2	0.03984 (4)	0.54045 (9)	0.79226 (9)	0.05280 (19)
N1	0.20327 (12)	0.5025 (3)	0.7931 (3)	0.0443 (5)
H1	0.2409	0.4588	0.8434	0.053*
N2	0.43318 (12)	0.4245 (3)	0.6450 (2)	0.0425 (5)
N3	0.42916 (13)	0.2935 (3)	0.4527 (2)	0.0457 (5)
O1	0.41252 (11)	0.5735 (3)	1.1157 (2)	0.0586 (6)

O2	0.36494 (11)	0.5641 (3)	0.9022 (2)	0.0590 (6)
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*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0374 (11)	0.0372 (13)	0.0497 (15)	0.0009 (10)	0.0092 (11)	0.0018 (13)
C2	0.0522 (15)	0.0425 (15)	0.0518 (17)	−0.0023 (12)	0.0097 (13)	−0.0065 (14)
C3	0.0458 (14)	0.0469 (16)	0.063 (2)	−0.0076 (12)	0.0001 (13)	−0.0057 (16)
C4	0.0350 (12)	0.0496 (17)	0.062 (2)	−0.0056 (11)	0.0045 (12)	0.0027 (15)
C5	0.0362 (11)	0.0378 (13)	0.0472 (15)	0.0012 (10)	0.0104 (11)	0.0046 (12)
C6	0.0341 (10)	0.0344 (12)	0.0430 (14)	0.0025 (9)	0.0055 (10)	0.0047 (11)
C7	0.0293 (10)	0.0376 (13)	0.0472 (14)	0.0020 (9)	0.0119 (10)	0.0004 (12)
C8	0.0339 (11)	0.0495 (15)	0.0504 (16)	0.0006 (11)	0.0090 (11)	0.0030 (14)
C9	0.0402 (13)	0.0480 (16)	0.072 (2)	0.0062 (12)	0.0182 (14)	0.0166 (17)
C10	0.0468 (15)	0.0384 (15)	0.089 (3)	0.0036 (12)	0.0230 (16)	−0.0026 (17)
C11	0.0383 (12)	0.0468 (16)	0.067 (2)	−0.0010 (11)	0.0167 (13)	−0.0129 (15)
C12	0.0267 (10)	0.0422 (14)	0.0502 (15)	0.0005 (9)	0.0135 (10)	−0.0046 (12)
C13	0.0319 (11)	0.0561 (17)	0.0432 (15)	0.0005 (11)	0.0102 (10)	−0.0061 (14)
C14	0.0303 (10)	0.0338 (12)	0.0445 (14)	0.0008 (9)	0.0074 (10)	−0.0019 (11)
C15	0.0539 (14)	0.0419 (14)	0.0395 (14)	0.0020 (12)	0.0159 (12)	0.0026 (13)
C16	0.0441 (13)	0.0577 (18)	0.0356 (13)	−0.0024 (12)	0.0094 (11)	0.0018 (13)
C17	0.0451 (13)	0.0503 (16)	0.0493 (16)	0.0086 (12)	0.0096 (12)	0.0110 (14)
C18	0.0404 (12)	0.0432 (15)	0.0522 (17)	0.0056 (11)	0.0084 (12)	−0.0035 (13)
Ag1	0.04020 (13)	0.05477 (15)	0.03712 (13)	0.00513 (8)	0.01297 (8)	−0.00042 (10)
Cl1	0.0401 (3)	0.0555 (4)	0.0877 (6)	0.0068 (3)	0.0176 (3)	−0.0087 (5)
Cl2	0.0458 (3)	0.0534 (4)	0.0647 (5)	0.0013 (3)	0.0243 (3)	−0.0020 (4)
N1	0.0344 (10)	0.0402 (12)	0.0504 (14)	0.0065 (9)	−0.0019 (9)	−0.0026 (11)
N2	0.0401 (10)	0.0500 (14)	0.0375 (11)	0.0031 (9)	0.0104 (9)	−0.0026 (11)
N3	0.0534 (13)	0.0460 (13)	0.0392 (12)	−0.0014 (10)	0.0149 (10)	−0.0015 (11)
O1	0.0334 (9)	0.0967 (19)	0.0426 (11)	0.0109 (10)	0.0049 (8)	0.0071 (12)
O2	0.0412 (10)	0.0880 (18)	0.0456 (12)	0.0186 (10)	0.0080 (9)	−0.0133 (12)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

C1—C2	1.379 (4)	C12—C13	1.504 (4)
C1—C6	1.390 (4)	C13—C14	1.537 (3)
C1—Cl1	1.739 (3)	C13—H13A	0.9700
C2—C3	1.387 (4)	C13—H13B	0.9700
C2—H2	0.9300	C14—O2	1.242 (4)
C3—C4	1.362 (5)	C14—O1	1.244 (3)
C3—H3	0.9300	C15—N2	1.320 (4)
C4—C5	1.382 (4)	C15—N3	1.333 (4)
C4—H4	0.9300	C15—H15	0.9300
C5—C6	1.409 (3)	C16—N3	1.338 (4)
C5—Cl2	1.733 (3)	C16—C17	1.367 (5)
C6—N1	1.387 (3)	C16—H16	0.9300
C7—C8	1.382 (4)	C17—C18	1.388 (5)
C7—C12	1.394 (4)	C17—H17	0.9300



C7—N1	1.426 (4)	C18—N2	1.330 (4)
C8—C9	1.383 (5)	C18—H18	0.9300
C8—H8	0.9300	Ag1—O2	2.279 (2)
C9—C10	1.375 (6)	Ag1—O1 <sup>i</sup>	2.280 (2)
C9—H9	0.9300	Ag1—N2	2.381 (3)
C10—C11	1.380 (5)	Ag1—N3 <sup>ii</sup>	2.412 (3)
C10—H10	0.9300	Ag1—Ag1 <sup>i</sup>	2.8931 (5)
C11—C12	1.383 (4)	N1—H1	0.8600
C11—H11	0.9300		
C2—C1—C6	123.5 (2)	C12—C13—H13B	108.5
C2—C1—C11	118.0 (2)	C14—C13—H13B	108.5
C6—C1—C11	118.5 (2)	H13A—C13—H13B	107.5
C1—C2—C3	118.8 (3)	O2—C14—O1	125.6 (2)
C1—C2—H2	120.6	O2—C14—C13	118.5 (2)
C3—C2—H2	120.6	O1—C14—C13	115.9 (3)
C4—C3—C2	120.1 (3)	N2—C15—N3	126.6 (3)
C4—C3—H3	119.9	N2—C15—H15	116.7
C2—C3—H3	119.9	N3—C15—H15	116.7
C3—C4—C5	120.3 (3)	N3—C16—C17	122.1 (3)
C3—C4—H4	119.9	N3—C16—H16	118.9
C5—C4—H4	119.9	C17—C16—H16	118.9
C4—C5—C6	122.0 (3)	C16—C17—C18	117.2 (3)
C4—C5—C12	117.6 (2)	C16—C17—H17	121.4
C6—C5—C12	120.5 (2)	C18—C17—H17	121.4
N1—C6—C1	121.9 (2)	N2—C18—C17	121.4 (3)
N1—C6—C5	122.8 (3)	N2—C18—H18	119.3
C1—C6—C5	115.2 (2)	C17—C18—H18	119.3
C8—C7—C12	120.6 (3)	O2—Ag1—O1 <sup>i</sup>	148.04 (10)
C8—C7—N1	121.4 (3)	O2—Ag1—N2	99.71 (8)
C12—C7—N1	118.1 (2)	O1 <sup>i</sup> —Ag1—N2	89.58 (8)
C7—C8—C9	120.5 (3)	O2—Ag1—N3 <sup>ii</sup>	97.48 (9)
C7—C8—H8	119.8	O1 <sup>i</sup> —Ag1—N3 <sup>ii</sup>	108.69 (9)
C9—C8—H8	119.8	N2—Ag1—N3 <sup>ii</sup>	107.93 (9)
C10—C9—C8	119.7 (3)	O2—Ag1—Ag1 <sup>i</sup>	81.70 (6)
C10—C9—H9	120.2	O1 <sup>i</sup> —Ag1—Ag1 <sup>i</sup>	76.19 (6)
C8—C9—H9	120.2	N2—Ag1—Ag1 <sup>i</sup>	151.80 (6)
C9—C10—C11	119.4 (3)	N3 <sup>ii</sup> —Ag1—Ag1 <sup>i</sup>	99.73 (6)
C9—C10—H10	120.3	C6—N1—C7	123.3 (2)
C11—C10—H10	120.3	C6—N1—H1	118.4
C10—C11—C12	122.2 (3)	C7—N1—H1	118.4
C10—C11—H11	118.9	C15—N2—C18	116.7 (3)
C12—C11—H11	118.9	C15—N2—Ag1	122.4 (2)
C11—C12—C7	117.6 (3)	C18—N2—Ag1	120.8 (2)
C11—C12—C13	120.6 (3)	C15—N3—C16	115.9 (3)
C7—C12—C13	121.9 (2)	C15—N3—Ag1 <sup>iii</sup>	116.2 (2)
C12—C13—C14	114.9 (2)	C16—N3—Ag1 <sup>iii</sup>	127.6 (2)
C12—C13—H13A	108.5	C14—O1—Ag1 <sup>i</sup>	125.2 (2)

C14—C13—H13A	108.5	C14—O2—Ag1	117.96 (17)
C6—C1—C2—C3	−0.1 (5)	N1—C7—C12—C13	2.6 (4)
C11—C1—C2—C3	−180.0 (3)	C11—C12—C13—C14	−105.3 (3)
C1—C2—C3—C4	−2.0 (5)	C7—C12—C13—C14	75.6 (3)
C2—C3—C4—C5	0.7 (5)	C12—C13—C14—O2	−31.7 (4)
C3—C4—C5—C6	2.7 (5)	C12—C13—C14—O1	149.1 (3)
C3—C4—C5—C12	−175.9 (3)	N3—C16—C17—C18	−0.5 (4)
C2—C1—C6—N1	179.0 (3)	C16—C17—C18—N2	0.5 (4)
C11—C1—C6—N1	−1.2 (4)	C1—C6—N1—C7	133.5 (3)
C2—C1—C6—C5	3.2 (4)	C5—C6—N1—C7	−51.1 (4)
C11—C1—C6—C5	−176.9 (2)	C8—C7—N1—C6	−21.6 (4)
C4—C5—C6—N1	179.8 (3)	C12—C7—N1—C6	157.8 (3)
C12—C5—C6—N1	−1.6 (4)	N3—C15—N2—C18	−0.3 (4)
C4—C5—C6—C1	−4.5 (4)	N3—C15—N2—Ag1	−176.8 (2)
C12—C5—C6—C1	174.0 (2)	C17—C18—N2—C15	−0.1 (4)
C12—C7—C8—C9	−1.8 (4)	C17—C18—N2—Ag1	176.4 (2)
N1—C7—C8—C9	177.6 (3)	N2—C15—N3—C16	0.3 (4)
C7—C8—C9—C10	−0.2 (4)	N2—C15—N3—Ag1 <sup>iii</sup>	173.7 (2)
C8—C9—C10—C11	1.0 (5)	C17—C16—N3—C15	0.2 (4)
C9—C10—C11—C12	0.2 (5)	C17—C16—N3—Ag1 <sup>iii</sup>	−172.4 (2)
C10—C11—C12—C7	−2.1 (4)	O2—C14—O1—Ag1 <sup>i</sup>	17.1 (4)
C10—C11—C12—C13	178.7 (3)	C13—C14—O1—Ag1 <sup>i</sup>	−163.8 (2)
C8—C7—C12—C11	3.0 (4)	O1—C14—O2—Ag1	18.3 (4)
N1—C7—C12—C11	−176.5 (2)	C13—C14—O2—Ag1	−160.8 (2)
C8—C7—C12—C13	−177.9 (2)		

Symmetry codes: (i)  $-x+1, -y+1, -z+2$ ; (ii)  $x, -y+1/2, z+1/2$ ; (iii)  $x, -y+1/2, z-1/2$ .

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg6 is the centroid of the [please define] ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O2	0.86	2.43	2.971 (3)	122
C16—H16 $\cdots$ O1 <sup>iv</sup>	0.93	2.51	3.248 (4)	136
C13—H13B $\cdots$ Cg6 <sup>iii</sup>	0.97	3.30	3.983 (3)	129

Symmetry codes: (iii)  $x, -y+1/2, z-1/2$ ; (iv)  $x, y, z-1$ .