

Poly[(μ_3 -*N*-acetyl-L-histidinato- κ^4 N,O:O:O')silver(I)]

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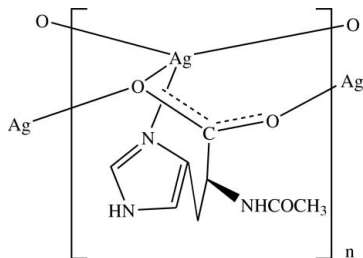
Received 24 August 2007; accepted 24 August 2007

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.028; wR factor = 0.064; data-to-parameter ratio = 12.8.

The 1:2 molar ratio reaction of Ag_2O with *N*-acetyl-L-histidine (H_2achis) possessing the partial structure $\text{O}=\text{C}-\text{N}-\text{C}-\text{COOH}$, as well as imidazole units, afforded the light-stable and water-insoluble silver(I) title complex, $[\text{Ag}(\text{C}_8\text{H}_{10}\text{N}_3\text{O}_3)]_n$. This complex showed modest antimicrobial activity against selected bacteria and yeasts in a water-suspension system. X-ray crystallography revealed that the complex in the solid state forms a helical polymeric structure with an AgNO_3 core based on chelating Hachis^- (one carboxylate O atom and one imidazole N atom) and two O atoms of the other two Hachis^- ligands that can be described as $\infty\{[\text{Ag}(\text{Hachis})]\}$; this differs from the structure of the related silver(I) complex $\infty\{[\text{Ag}(\text{Hhis})]\}$ (*L*-histidine = H_2his) based on an AgN_2 core. Polymer chains of the title complex form three-dimensional intermolecular hydrogen-bonding networks in the crystal structure.

Related literature

For related literature, see: Gimeno & Laguna (2004); Huang *et al.* (2006); Kasuga *et al.* (2006); Masciocchi *et al.* (1995); Nomiya *et al.* (1997, 2000).



Experimental

Crystal data

$[\text{Ag}(\text{C}_8\text{H}_{10}\text{N}_3\text{O}_3)]$
 $M_r = 304.06$

Orthorhombic, $P2_12_12_1$
 $a = 5.039$ (3) Å

$b = 13.656$ (8) Å
 $c = 14.043$ (9) Å
 $V = 966.4$ (10) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 2.08$ mm⁻¹
 $T = 173$ (2) K
 $0.32 \times 0.29 \times 0.01$ mm

Data collection

Rigaku Mercury diffractometer
Absorption correction: numerical
(*ABSCOR*; Higashi, 1999)
 $T_{\min} = 0.556$, $T_{\max} = 0.980$

9224 measured reflections
1765 independent reflections
1715 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.064$
 $S = 1.11$
1765 reflections
138 parameters
H-atom parameters not refined

$\Delta\rho_{\max} = 0.80$ e Å⁻³
 $\Delta\rho_{\min} = -0.65$ e Å⁻³
Absolute structure: Flack (1983),
with 707 Friedel pairs
Flack parameter: -0.03 (5)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2N}\cdots\text{O1}^i$	0.88	2.02	2.834 (5)	153

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

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by a High-tech Research Center Project from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2285).

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supplementary materials

Acta Cryst. (2007). E63, m2440 [doi:10.1107/S1600536807041724]

Poly[(μ_3 -*N*-acetyl-*L*-histidinato- κ^4 N,O:O:O')silver(I)]

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Comment

Although Ag—N and Ag—O bonding complexes are potential bioinorganic materials such as antimicrobial activities (Gimeno *et al.*, 2004.), light-sensitivity and poor solubility made them harder to be handled. Their crystallization was not easy. Silver imidazolite $\infty\{[\text{Ag}(\text{im})]\}$ (Him=imidazole), which showed strongly effective and a wide spectrum of antimicrobial activities but insoluble in most solvents (Nomiya *et al.*, 1997.), was structurally characterized by powder X-ray diffraction (Masciocchi *et al.*, 1995.) and its single crystals were prepared by hydrothermal method only in 2006 (Huang *et al.*, 2006.). Recently, we noticed that reactions of Ag₂O with ligands having an OOC-C—X (X=N or O)—C=O moiety (such as 2-pyrrolidone-5-carboxylic acid, 5-oxo-2-tetrahydrofuran-2-carboxylic acid, camphanic acid, and *N*-acetyl-glycine) afforded water-soluble and relatively light-stable (*i.e.* stable for a few hours to days at ambient temperature) Ag—O bonding complexes (Kasuga *et al.*, 2006, and references therein). Herein, we report crystal structure of the (*N*-acetyl-*L*-histidinato)silver(I) (complex 1), whose ligand containing both the OOC-C—N—C=O moiety and imidazole ring (Fig. 1).

Reaction of *N*-acetyl-*L*-histidine (H₂achis) and Ag₂O at ambient temperature in water followed by the vapor-diffusion crystallization gave water-insoluble complex 1, which showed modest antimicrobial activities against *E. coli*, *B. subtilis*, *P. aeruginosa*, *C. albicans* and *S. cerevisiae* in water-suspension system.

The closely related complex, water-insoluble $\infty\{[\text{Ag}(\text{Hhis})]\}$ (H₂his=*L*-histidine), was a helical polymer consisting of a bent 2-coordinate silver(I) atom linking with the N_{amino} atom in one Hhis[−] ligand and the N π atom of imidazole in a different Hhis[−] ligand (Nomiya *et al.*, 2000). In complex 1, N π atom also coordinated to Ag1, but N_{amido} atom did not. Instead, an oxygen atom (O2) of the carboxylate group and two oxygen atoms (O1ⁱ and O2ⁱⁱ) in different Hachis[−] ligands coordinated to Ag1 (symmetry codes: (i) $x + 1/2, -y + 1/2, -z + 2$; (ii) $x - 1/2, -y + 1/2, -z + 2$). Therefore, the geometry around Ag1 was disordered 4-coordinate with AgN₁O₃ core (Fig. 2). The O2 in complex 1 was bridged by two silver(I) atoms (Ag1 and Ag1ⁱ). The six-membered ring formed by Ag1, O2ⁱⁱ, Ag1ⁱⁱ, O1, C1 and O2 was connected through silver(I) and O2 atoms to form ladder polymer chain of $\infty\{[\text{Ag}(\text{Hachis})]\}$ across the *a* axis. The distance and angle of N2—H2N \cdots O1ⁱⁱⁱ indicated that hydrogen bond was formed between carboxylate and imidazole ring (symmetry code: (iii) $-x + 1/2, -y, z - 1/2$). For one pitch of the chain, four hydrogen bonds were observed as shown in dashed lines in Fig. 3.

In summary, $\infty\{[\text{Ag}(\text{Hachis})]\}$ is a ladder polymer, which forms three-dimensional network of hydrogen bonds between the ladders chains.

Experimental

To a suspension of 116 mg (0.5 mmol) of Ag₂O in 20 ml of water was added 198 mg of H₂achis (0.5 mmol), followed by stirring for 1 h at room temperature. The black suspension changed to a clear, colorless solution and the solution was filtered through a folded filter paper (Whatman #5). Vapor diffusion was performed at room temperature by using the

supplementary materials

colorless filtrate as the inner solution and acetone as the external solvent. The colorless platelet crystals that were formed were collected on a membrane filter (JG 0.2 mm) and they were washed with acetone and ether (50 ml each) (0.1375 g of $\infty\{[\text{Ag}(\text{Hachis})]\}$ (complex 1), 90.4% yield).

Complex 1 is insoluble in H_2O and other organic solvents (MeOH, DMSO, acetone, EtOH, CH_3CN , CH_2Cl_2 , CHCl_3 , ether, and EtOAc). The color of the crystals did not change for at least two weeks. Complex 1 was characterized by EA, IR, and TG/DTA.

Prominent IR bands at $1800\text{--}400\text{ cm}^{-1}$ (KBr) 1629_{vs} , 1590_{vs} , 1438_{w} , 1399_{m} , 1297_{w} , 1105_{w} , 1087_{w} , 939_{w} , 692_{s} , 663_{s} , 622_{s} , 552_{s} . No weight loss before decomposition (*ca* $226\text{ }^\circ\text{C}$). Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{N}_3\text{O}_3\text{Ag}$. C 31.60, H 3.32, N 13.82. Found (Perkin Elmer PE2400 series II CHNS/O Analyzer) C 31.59, H 2.79, N 13.77.

Complex 1 showed modest activity against Gram-negative bacteria (minimum inhibitory concentration (=MIC) for *E. coli* and *P. aeruginosa* was both $250\text{ }\mu\text{g mL}^{-1}$), Gram-positive bacterium (MIC for *B. subtilis* was $500\text{ }\mu\text{g mL}^{-1}$) and yeasts (MIC for *C. albicans* and *S. cerevisiae* was both $125\text{ }\mu\text{g mL}^{-1}$).

Refinement

The H atoms were placed at geometrically calculated positions and refined using riding and rotating models.

Figures

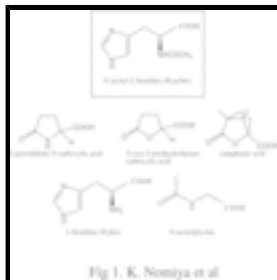


Fig. 1. Chemical structures of H₂achis and the related ligands.

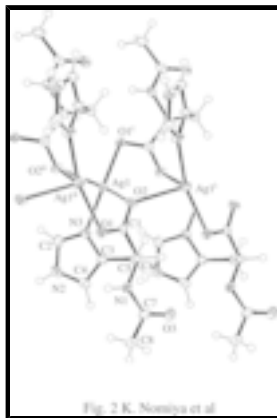


Fig. 2. ORTEP-3 drawing (Farrugia, 1997) of complex 1 with 50% probability thermal ellipsoids.

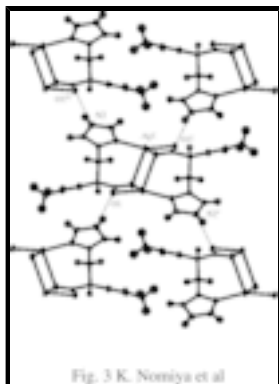


Fig. 3. Hydrogen bonding network of complex 1 viewed along the a axis. Symmetry codes: (i) $x + 1/2, -y + 1/2, -z + 2$, (ii) $x - 1/2, -y + 1/2, -z + 2$ and (iii) $-x + 1/2, -y, z - 1/2$.

Poly[(μ_3 -*N*-acetyl-*L*-histidinato- κ^4 N,O:O:O')silver(I)]

Crystal data

[Ag(C₈H₁₀N₃O₃)]

$M_r = 304.06$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.039$ (3) Å

$b = 13.656$ (8) Å

$c = 14.043$ (9) Å

$V = 966.4$ (10) Å³

$Z = 4$

$F_{000} = 600$

$D_x = 2.090$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 86 reflections

$\theta = 3.3$ – 25.4°

$\mu = 2.08$ mm⁻¹

$T = 173$ (2) K

Prism, colorless

$0.32 \times 0.29 \times 0.01$ mm

Data collection

Rigaku Mercury
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 14.892 pixels mm⁻¹

$T = 173$ (2) K

dtcell.ref scans

Absorption correction: Numerical
(ABSCOR; Higashi, 1999)

$T_{\min} = 0.556, T_{\max} = 0.980$

9224 measured reflections

1765 independent reflections

1715 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\text{max}} = 25.4^\circ$

$\theta_{\text{min}} = 3.3^\circ$

$h = -6 \rightarrow 6$

$k = -16 \rightarrow 15$

$l = -16 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.9828P]$

supplementary materials

$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{\max} = 0.001$
1765 reflections	$\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$
138 parameters	$\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), with 0000 Friedel pairs
	Flack parameter: $-0.03 (5)$

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5974 (8)	0.1081 (3)	1.0856 (3)	0.0156 (9)
C2	0.3599 (10)	0.0856 (3)	0.7963 (3)	0.0246 (10)
H2	0.2450	0.1308	0.7656	0.030*
C3	0.6681 (9)	0.0232 (3)	0.8858 (3)	0.0186 (8)
C4	0.5516 (9)	-0.0520 (3)	0.8383 (3)	0.0230 (10)
H4	0.5955	-0.1194	0.8433	0.028*
C5	0.8765 (8)	0.0227 (3)	0.9608 (3)	0.0194 (9)
H5A	0.9866	0.0823	0.9538	0.023*
H5B	0.9933	-0.0347	0.9506	0.023*
C6	0.7665 (8)	0.0188 (3)	1.0637 (3)	0.0171 (9)
H6	0.9228	0.0211	1.1076	0.021*
C7	0.7649 (8)	-0.1554 (3)	1.1000 (3)	0.0237 (9)
C8	0.6020 (9)	-0.2448 (3)	1.1236 (3)	0.0294 (10)
H8A	0.4149	-0.2318	1.1094	0.044*
H8B	0.6215	-0.2603	1.1914	0.044*
H8C	0.6638	-0.3003	1.0853	0.044*
Ag1	0.66858 (6)	0.25670 (2)	0.89688 (2)	0.02431 (11)
N1	0.6274 (7)	-0.0723 (2)	1.0830 (2)	0.0186 (7)
H1N	0.4528	-0.0734	1.0835	0.022*
N2	0.3583 (8)	-0.0117 (3)	0.7818 (3)	0.0264 (8)
H2N	0.2522	-0.0438	0.7430	0.032*
N3	0.5423 (8)	0.1095 (3)	0.8590 (3)	0.0217 (8)
O1	0.3590 (6)	0.09409 (18)	1.1138 (2)	0.0205 (6)
O2	0.6944 (6)	0.1908 (2)	1.0741 (2)	0.0239 (7)

O3 1.0065 (6) -0.1576 (2) 1.0979 (2) 0.0282 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.018 (2)	0.0183 (19)	0.011 (2)	0.0011 (16)	-0.0047 (16)	0.0001 (15)
C2	0.026 (2)	0.027 (2)	0.021 (2)	-0.006 (2)	-0.006 (2)	0.0099 (18)
C3	0.021 (2)	0.0176 (18)	0.017 (2)	0.0004 (17)	0.001 (2)	-0.0021 (16)
C4	0.027 (3)	0.020 (2)	0.022 (2)	-0.0045 (19)	0.0021 (18)	-0.0050 (17)
C5	0.015 (2)	0.019 (2)	0.024 (2)	0.0019 (17)	0.0018 (18)	-0.0012 (17)
C6	0.019 (2)	0.016 (2)	0.017 (2)	0.0004 (16)	0.0004 (16)	0.0004 (16)
C7	0.026 (2)	0.020 (2)	0.025 (2)	0.0069 (16)	-0.001 (2)	-0.002 (2)
C8	0.031 (2)	0.016 (2)	0.041 (3)	0.0042 (19)	-0.0045 (18)	0.002 (2)
Ag1	0.02532 (17)	0.01610 (16)	0.03151 (18)	-0.00361 (14)	-0.00139 (14)	0.00172 (14)
N1	0.0122 (17)	0.0166 (16)	0.027 (2)	0.0041 (14)	-0.0002 (15)	0.0010 (14)
N2	0.026 (2)	0.0271 (19)	0.026 (2)	-0.0082 (19)	-0.0051 (18)	-0.0035 (15)
N3	0.024 (2)	0.0180 (18)	0.0229 (18)	-0.0042 (16)	-0.0052 (16)	0.0009 (15)
O1	0.0163 (15)	0.0152 (13)	0.0301 (17)	0.0006 (11)	0.0041 (15)	0.0047 (12)
O2	0.0212 (15)	0.0167 (14)	0.0337 (17)	-0.0049 (13)	0.0023 (14)	0.0009 (12)
O3	0.0208 (16)	0.0263 (16)	0.0376 (18)	0.0061 (13)	-0.0010 (17)	-0.0043 (16)

Geometric parameters (Å, °)

C1—O2	1.241 (5)	C6—N1	1.454 (5)
C1—O1	1.279 (5)	C6—H6	1.0000
C1—C6	1.519 (6)	C7—O3	1.218 (5)
C2—N3	1.313 (6)	C7—N1	1.350 (5)
C2—N2	1.345 (5)	C7—C8	1.508 (6)
C2—H2	0.9500	C8—H8A	0.9800
C3—C4	1.358 (6)	C8—H8B	0.9800
C3—N3	1.390 (5)	C8—H8C	0.9800
C3—C5	1.488 (6)	Ag1—N3	2.174 (4)
C4—N2	1.371 (6)	Ag1—O1 ⁱ	2.257 (3)
C4—H4	0.9500	Ag1—O2 ⁱⁱ	2.528 (3)
C5—C6	1.548 (6)	Ag1—O2	2.649 (3)
C5—H5A	0.9900	N1—H1N	0.8800
C5—H5B	0.9900	N2—H2N	0.8800
O2—C1—O1	123.1 (4)	N1—C7—C8	116.1 (4)
O2—C1—C6	118.9 (4)	C7—C8—H8A	109.5
O1—C1—C6	118.0 (3)	C7—C8—H8B	109.5
N3—C2—N2	110.6 (4)	H8A—C8—H8B	109.5
N3—C2—H2	124.7	C7—C8—H8C	109.5
N2—C2—H2	124.7	H8A—C8—H8C	109.5
C4—C3—N3	108.1 (4)	H8B—C8—H8C	109.5
C4—C3—C5	130.5 (4)	N3—Ag1—O1 ⁱ	160.48 (13)
N3—C3—C5	121.2 (3)	N3—Ag1—O2 ⁱⁱ	91.43 (13)
C3—C4—N2	106.8 (4)	O1 ⁱ —Ag1—O2 ⁱⁱ	99.02 (10)
C3—C4—H4	126.6	N3—Ag1—O2	86.01 (12)

supplementary materials

N2—C4—H4	126.6	O1 ⁱ —Ag1—O2	110.37 (10)
C3—C5—C6	114.1 (3)	O2 ⁱⁱ —Ag1—O2	89.49 (9)
C3—C5—H5A	108.7	C7—N1—C6	120.3 (4)
C6—C5—H5A	108.7	C7—N1—H1N	119.9
C3—C5—H5B	108.7	C6—N1—H1N	119.9
C6—C5—H5B	108.7	C2—N2—C4	107.7 (4)
H5A—C5—H5B	107.6	C2—N2—H2N	126.2
N1—C6—C1	112.3 (3)	C4—N2—H2N	126.2
N1—C6—C5	112.0 (3)	C2—N3—C3	106.8 (3)
C1—C6—C5	111.2 (3)	C2—N3—Ag1	126.8 (3)
N1—C6—H6	107.0	C3—N3—Ag1	125.7 (3)
C1—C6—H6	107.0	C1—O1—Ag1 ⁱⁱ	104.1 (2)
C5—C6—H6	107.0	C1—O2—Ag1 ⁱ	127.5 (3)
O3—C7—N1	122.0 (4)	C1—O2—Ag1	114.4 (2)
O3—C7—C8	121.9 (4)	Ag1 ⁱ —O2—Ag1	95.84 (10)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N \cdots O1 ⁱⁱⁱ	0.88	2.02	2.834 (5)	153

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

Fig. 1

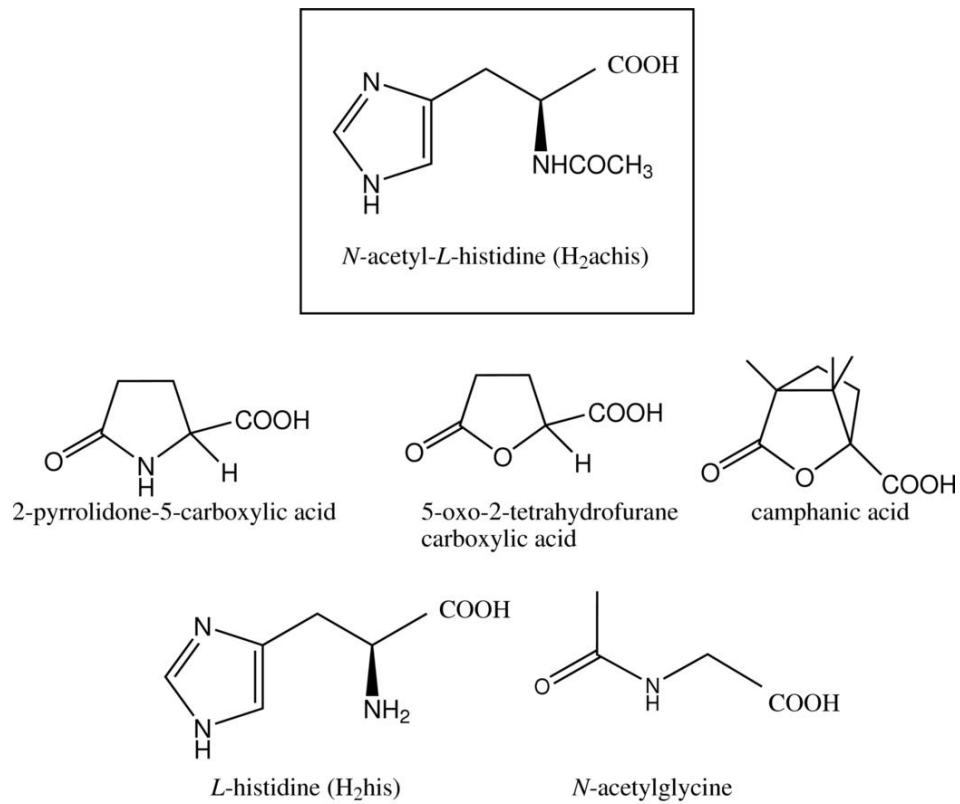


Fig 1. K. Nomiya et al

Fig. 2

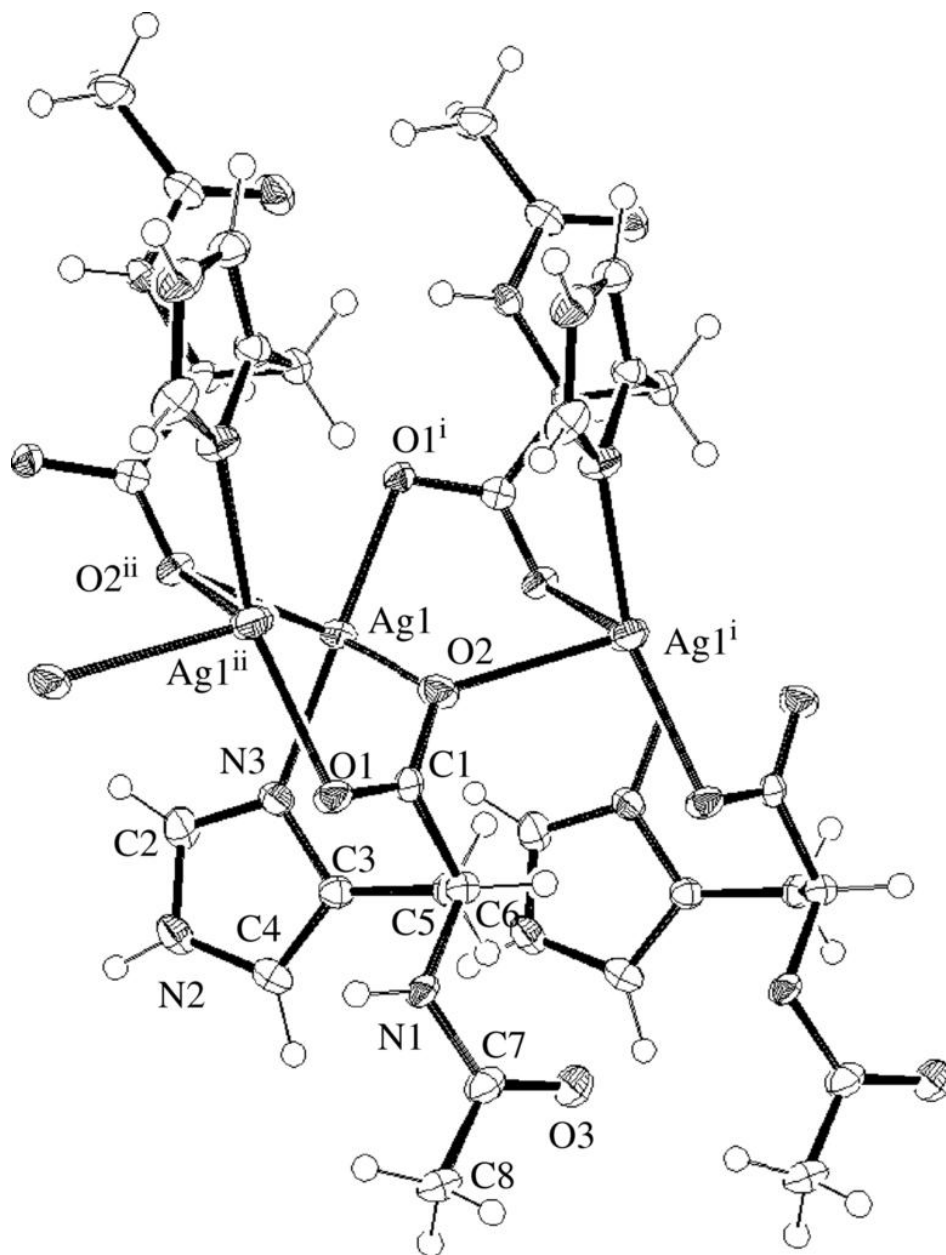


Fig. 2 K. Nomiya et al

Fig. 3

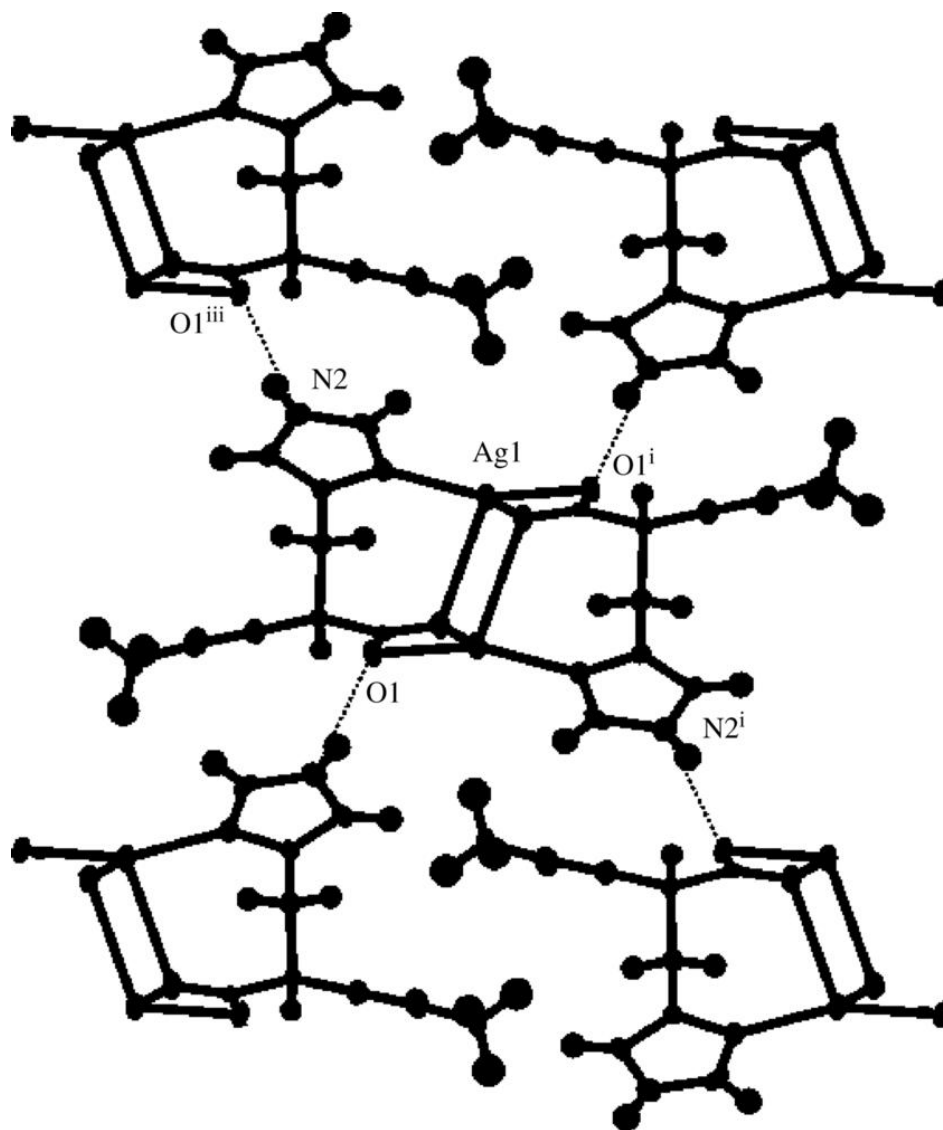


Fig. 3 K. Nomiya et al