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Key indicators

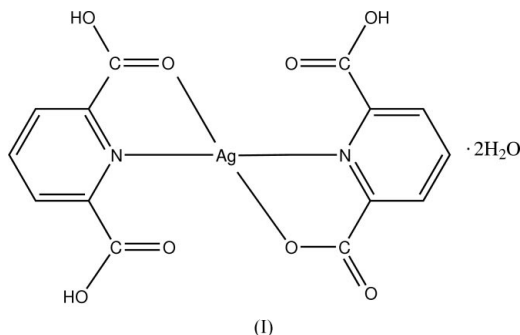
Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.025
 wR factor = 0.079
Data-to-parameter ratio = 14.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.(6-Carboxylatopyridine-2-carboxylic acid- $\kappa^2\text{N},\text{O}$)-
(pyridine-2,6-dicarboxylic acid- $\kappa^2\text{N},\text{O}$)silver(I)
dihydrateIn the title compound, $[\text{Ag}(\text{C}_7\text{H}_4\text{NO}_4)(\text{C}_7\text{H}_5\text{NO}_4)] \cdot 2\text{H}_2\text{O}$, the Ag^{I} atom has a distorted tetrahedral coordination geometry, defined by two pyridyl N and two carboxyl O atoms from bidentate ligands in a *trans* arrangement. The planar ligands in the complex are almost perpendicular to each other. The complexes are connected *via* symmetric $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds and linked through the water molecules, forming a three-dimensional network.

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Comment

Dipicolinic acid (H_2dpa , pyridine-2,6-dicarboxylic acid), which is present in the viscous matter of Natto, a Japanese food, is desirable because of its low toxicity (Nadai *et al.*, 1995) and its biological activity (Setlow & Setlow, 1993). Metal complexes of this ligand have been extensively studied because of its ability to form stable chelates (Ducommun *et al.*, 1989) with different coordination modes, such as bidentate (Zhou & Kostic, 1988) or bridging (Sengupta *et al.*, 1983). A series of isomorphous dipicolinate lanthanide complexes were synthesized (Fernandes *et al.*, 2001) and the structures were reported together with their activities as electron carriers in model biological systems (Pope *et al.*, 1981). Two silver complexes of dipicolinic acid have been reported: one was published (Drew *et al.*, 1970) with structural information on the Ag^{II} complex $[\text{Ag}(\text{H}_2\text{dpa})(\text{dpa})] \cdot \text{H}_2\text{O}$ (II), while the second example was a polymeric Ag^{I} compound, $[\text{NH}_4[\text{Ag}(\text{dpa})] \cdot 2\text{H}_2\text{O}]_n$. In spite of being described as a five-coordinate pentagonal planar unit repeating in a sheet polymer structure (Smith & Reddy, 1994), it could not be satisfactorily refined and so its precise structure is not clear. We report here the crystal structure of the title compound, $[\text{Ag}(\text{H}_2\text{dpa})(\text{Hdpa})] \cdot 2\text{H}_2\text{O}$ (I).The structure of (I) is depicted in Fig. 1. Each dpa ligand acts as a bidentate ligand of Ag^{I} , through the pyridine N and one of the carboxyl O atoms. Both ligand molecules are nearly planar, as seen from the $\text{N}-\text{C}-\text{C}-\text{O}$ torsion angles (Table 1). The $\text{O}-\text{Ag}-\text{N}$ chelate angles $[68.78(8)-69.24(7)^\circ]$

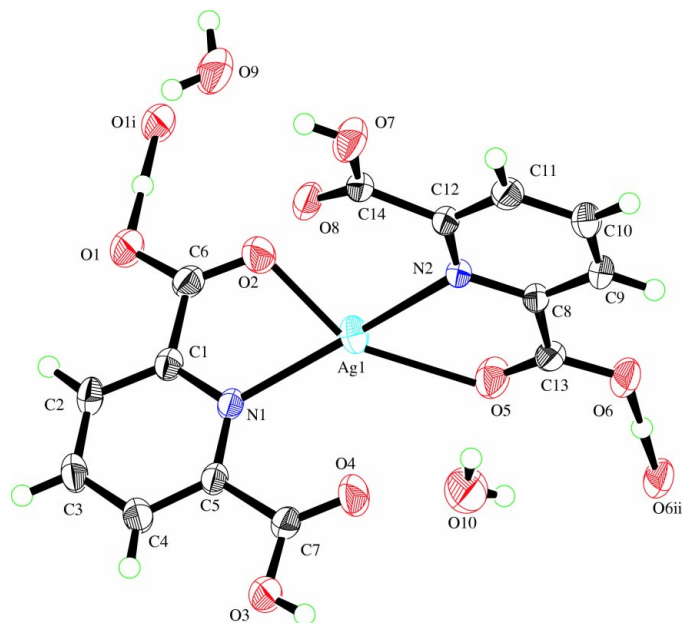


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. [Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $2 - x, 1 - y, 1 - z$.]

are somewhat smaller than those observed in (II) [76.1 and 70.6°; Drew *et al.*, 1970]. The central Ag^I atom lies in a deformed tetrahedral coordination geometry, in which the two pyridine rings have a dihedral angle of 79.93 (10)°. Regarding the silver coordination environment, the interaction between Ag1–N1/N2 is stronger than Ag1–O2/O5. The Ag1···O4/O8 distances are 2.765 (2)–2.768 (2) Å, suggesting weak interactions. As a result of the different coordination strengths of the carboxyl O atoms, the C6–O2 bond distance of 1.225 (3) Å is slightly longer than C7–O4 of 1.197 (3) Å. The same phenomenon is seen in the other ligand molecule.

The two ligand molecules have almost the same coordinate mode in (I), with one of the two carboxy groups deprotonated and forming a symmetric hydrogen bond (Table 2) with a carboxy group of a neighboring complex. This is different from (II), where one of two ligands is anionic, with Ag–N = 2.08 Å and Ag–O = 2.2 Å, and another is neutral, with Ag–N = 2.2 Å and Ag–O = 2.54 Å (Drew *et al.*, 1970). Atoms H5 and H10 in (I) lie on centres of symmetry and are involved in O1–H5···O1ⁱ and O6–H10···O6ⁱⁱ hydrogen bonds [symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $2 - x, 1 - y, 1 - z$], and the O–H bond distances are 1.23 and 1.24 Å. Via these strong O–H···O hydrogen bonds, adjacent complexes are linked to each other and extend to form a stable cluster with a three-dimensional hydrogen-bonding network through the water molecules. This packing mode was first observed in a metal-dpa compound.

Experimental

Thin colorless Block-shaped crystals of (I) were obtained by slow evaporation of an aqueous solution of a mixture of dipicolinic acid and AgNO₃ (molar ratio 5:1) at room temperature.

Crystal data

[Ag(C₇H₄NO₄)(C₇H₅NO₄)]·2H₂O
M_r = 477.13
 Triclinic, *P* $\bar{1}$
a = 6.934 (9) Å
b = 8.103 (8) Å
c = 15.10 (2) Å
 α = 95.92 (4)°
 β = 102.76 (5)°
 γ = 98.04 (4)°
V = 811.4 (17) Å³

Z = 2
D_x = 1.953 Mg m⁻³
 Mo K α radiation
 Cell parameters from 7457 reflections
 θ = 3.0–27.5°
 μ = 1.31 mm⁻¹
T = 296.1 K
 Block, colorless
 0.30 × 0.10 × 0.10 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.676, *T_{max}* = 0.881
 7969 measured reflections

3685 independent reflections
 3326 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.019
 θ_{max} = 27.5°
h = –8 → 8
k = –10 → 10
l = –19 → 19

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.079$
S = 1.11
 3685 reflections
 256 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.3231P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.003$
 $\Delta\rho_{max} = 0.59 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.51 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ag1–N1	2.326 (2)	O2–C6	1.225 (3)
Ag1–N2	2.326 (2)	O3–C7	1.314 (3)
Ag1–O2	2.504 (2)	O4–C7	1.197 (3)
Ag1–O4	2.768 (2)	O5–C13	1.226 (3)
Ag1–O5	2.507 (2)	O6–C13	1.278 (3)
Ag1–O8	2.765 (2)	O7–C14	1.297 (3)
O1–C6	1.277 (3)	O8–C14	1.212 (3)
O2–Ag1–O5	120.32 (7)	O2–Ag1–N1	69.24 (7)
N1–Ag1–N2	155.06 (6)	O5–Ag1–N2	68.78 (8)
N1–C1–C6–O2	0.8 (4)	N2–C8–C13–O5	0.4 (3)
N1–C5–C7–O4	–0.5 (4)	N2–C12–C14–O8	–6.1 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H5···O1 ⁱ	1.23	1.23	2.454 (4)	180
O6–H10···O6 ⁱⁱ	1.24	1.24	2.482 (3)	180
O7–H9···O9	0.80	1.71	2.501 (3)	167
O10–H13···O5	0.86	1.86	2.713 (4)	170
O3–H4···O8 ⁱⁱⁱ	0.80	1.95	2.734 (3)	165
O9–H11···O2 ^{iv}	0.80	1.97	2.706 (3)	153
O9–H12···O10 ^v	0.89	1.89	2.749 (4)	161
O10–H14···O4 ^{vi}	0.73	2.65	3.084 (5)	120

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

All H atoms were located in difference Fourier maps and then were positioned geometrically. Atoms H5 and H10 lie on centers of symmetry, with O–H distances of 1.23 and 1.24 Å. The other H atoms bonded to O atoms were refined isotropically and fixed, the

O—H distances being 0.73–0.89 Å. Other H atoms were constrained to ride on their parent atoms, with C—H distances of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrystalStructure* (Rigaku & Rigaku/MS, 2000–2004) and *CRYSTALS* (Watkin *et al.*, 1996); cell refinement: *CrystalStructure* and *CRYSTALS*; data reduction: *CrystalStructure* and *CRYSTALS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994) and *DIRDIF* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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