



Crystal structure of a pyrazine-2,3-dicarboxamide ligand and of its silver(I) nitrate complex, a three-dimensional coordination polymer

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Received 11 April 2017

Accepted 27 April 2017

Edited by T. J. Prior, University of Hull, England

Keywords: crystal structure; carboxamide; pyrazine; pyridine; silver(I); Ag—Ag bond; three-dimensional coordination polymer; hydrogen bonding.

CCDC references: 1546645; 1546644

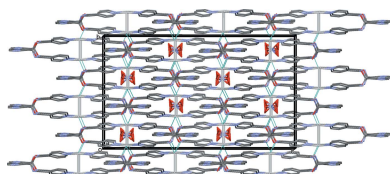
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The title ligand, $C_{18}H_{16}N_6O_2 \cdot 2H_2O$ (**L1**) [N^2, N^3 -bis(pyridin-4-ylmethyl)pyrazine-2,3-dicarboxamide], crystallized as a dihydrate. The molecule is U-shaped with the carboxamide groups being *cis* to one another, making a dihedral angle of $81.6(5)^\circ$. The terminal pyridine rings are inclined to one another by $58.5(4)^\circ$. There is an intramolecular $N-H \cdots N_{\text{pyrazine}}$ hydrogen bond present, forming an $S(5)$ ring motif. In the crystal, adjacent molecules are linked by $N-H \cdots O_{\text{carboxamide}}$ hydrogen bonds, forming a chain along $[001]$. A chain of hydrogen-bonded water molecules is linked to the chain of (**L1**) molecules by $O-H \cdots N$ hydrogen bonds, forming columns propagating along the *c* axis. The columns are linked by $C-H \cdots O$ and $C-H \cdots N$ hydrogen bonds, forming a three-dimensional supramolecular structure. The reaction of ligand (**L1**) with silver(I) nitrate led to the formation of a new three-dimensional coordination polymer, $\{[Ag(C_{18}H_{16}N_6O_2)]NO_3\}_n$, poly[[μ_4-N^2, N^3 -bis(pyridin-4-ylmethyl)pyrazine-2,3-dicarboxamide]silver(I) nitrate] (**I**). The asymmetric unit is composed of half of one silver ion, located on a twofold rotation axis, half a ligand molecule and half a positionally disordered nitrate anion located about a twofold rotation axis. The full molecule of the ligand is generated by twofold rotational symmetry, with this twofold axis bisecting the $C_{\text{ar}}-C_{\text{ar}}$ bonds of the pyrazine ring and the Ag—Ag bond. The carboxamide groups are now *trans* to one another, making a dihedral angle of $65.8(4)^\circ$. The two terminal pyridine rings are inclined to one another by $6.6(3)^\circ$. Two ligands wrap around an Ag—Ag bond of $3.1638(11)$ Å, forming a figure-of-eight-shaped complex molecule. Each silver ion is coordinated by two pyridine N atoms and by two carboxamide O atoms of neighbouring molecules, hence forming a three-dimensional framework. The nitrate anion is linked to the framework by $N-H \cdots O$ and $C-H \cdots O$ hydrogen bonds.

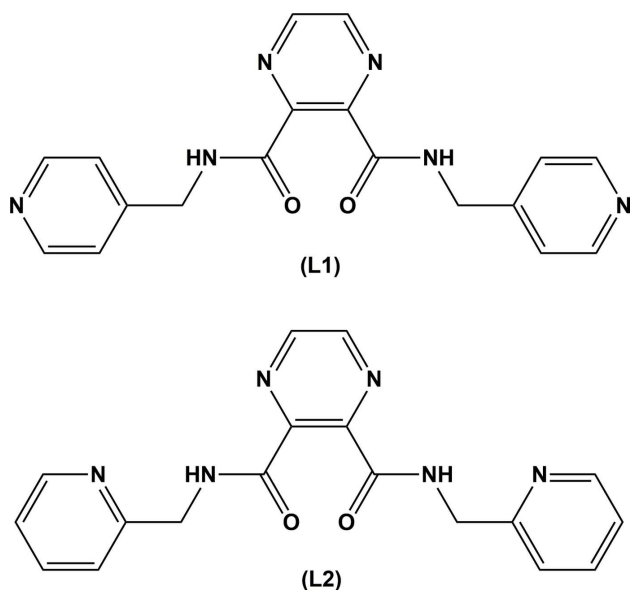
1. Chemical context

The title ligand, N^2, N^3 -bis(pyridin-4-ylmethyl)pyrazine-2,3-dicarboxamide (**L1**), is one of a series of ligands synthesized in order to study the superexchange in supramolecular complexes formed using pyrazine carboxamide derivatives and first row transition metal ions (Cati, 2002; Cati *et al.*, 2004). To the best of our knowledge, neither the synthesis nor the crystal structure of (**L1**) have been described previously. It is very similar to the ligand N^2, N^3 -bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamide (**L2**), for which a number of transition metal complexes have been described, including some interesting tetranuclear 2×2 grid-like and square complexes (Hausmann *et al.*, 2003; Klingele *et al.*, 2007). Two such complexes, $\{[Cu_4(\mathbf{L2})_4](ClO_4)_4\} \cdot 5CH_3OH \cdot 4H_2O$ and $\{[Ni_4(\mathbf{L2})_4]Cl_4\} \cdot 5CH_3CN \cdot 13H_2O$ (Cati *et al.*, 2004), exhibit



anion encapsulation, and magnetic susceptibility measurements indicate that they are weakly anti-ferromagnetic, with J values of -5.87 and -2.64 cm^{-1} , respectively.

A search of the Cambridge Structural Database (CSD; Groom *et al.*, 2016), indicated that silver nitrate is an excellent metal salt for the formation of multi-dimensional coordination polymers. The silver ion can have multiple coordination geometries and modes, and the nitrate anion has been shown to coordinate to metal ions in a number of different modes, many of which involve bridging metal ions. The properties of the complexes formed are extremely varied. For example, with the tetradentate ligand 1,6-bis(2*H*-1,2,3-triazol-2-yl)hexane, Huo *et al.* (2016) synthesized the three-dimensional coordination polymer, *catena*-[[μ -2,2'-(butane-1,4-diyl)bis(2*H*-1,2,3-triazole)]bis(μ -nitrate)disilver]. They showed that it exhibits highly selective and sensitive luminescence sensing of $\text{Cr}_2\text{O}_7^{2-}$ ions in aqueous solution. With the rigid tripodal arene-core-based nitrogen ligand, 1,3,5-tris(pyrazol-1-yl)benzene, Shu *et al.* (2006) formed a porous metal-organic framework, *viz.* *catena*-[bis(μ_3 -nitrate-*O,O',O''*)bis(μ_3 -1,3,5-tris(pyrazol-1-yl)benzene-*N,N',N''*)]trisilver(I) nitrate]. The nitrate counteranions located in the cationic framework can be exchanged reversibly without destruction of the structure. Hence, this compound can act as a zeolite-like porous material for anion exchange.

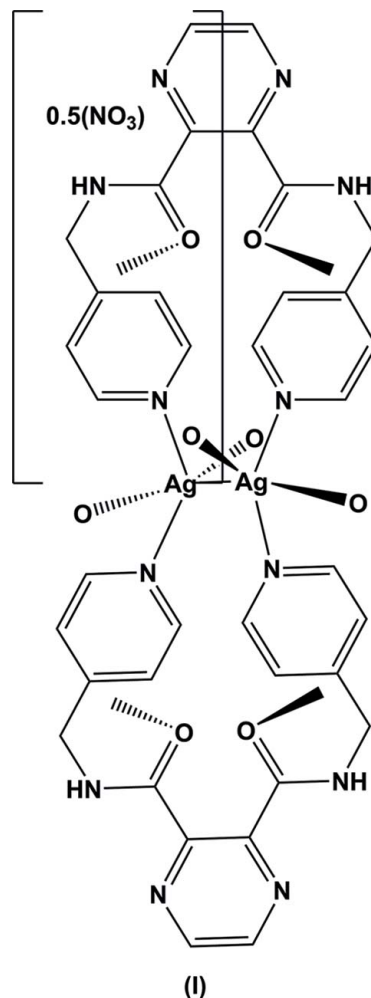


The title ligand has potentially two bidentate (N,N) and two monodentate ($\text{N}_{\text{pyridine}}$) coordination sites. It is therefore an interesting ligand to study its coordination behaviour with silver nitrate, and herein, we describe the solid state structures of ligand (**L1**), and the new three-dimensional coordination polymer, poly[[[μ_4 - N^2,N^3 -bis(pyridin-4-ylmethyl)pyrazine-2,3-dicarboxamide]silver(I)]nitrate] (**I**).

2. Structural commentary

The title ligand (**L1**) crystallized as a dihydrate, and its molecular structure is illustrated in Fig. 1. The molecule is U-

shaped with the carboxamide groups (C6/N3/C5/O1) being *cis* to one another, making a dihedral angle of 81.6 (5) $^\circ$. The terminal pyridine rings (N4/C7–C11) are inclined to one another by 58.5 (4) $^\circ$. There is an intramolecular N–H \cdots N hydrogen bond present, forming an *S*(5) ring motif (Fig. 1 and Table 1).



The reaction of the ligand with silver(I) nitrate led to the formation of a three-dimensional coordination polymer (**I**). The coordination of the ligand to the silver ions is illustrated in Fig. 2. Selected bond lengths and angles in (**I**) are given in Table 2. The asymmetric unit is composed of a silver ion, located on a twofold rotation axis, half a ligand molecule and half a nitrate anion. The full molecule of the ligand is generated by twofold rotational symmetry, with this twofold axis bisecting the C4–C4' bonds of the pyrazine ring and the Ag1–Ag1' bond (Table 2). The carboxamide groups (C6/N3/C5/O1) are now *trans* to one another, making a dihedral angle of 65.8 (4) $^\circ$. The terminal pyridine rings (N4/C7–C11) are inclined to one another by 6.6 (3) $^\circ$. Two ligands effectively wrap around a Ag–Ag bond of 3.1638 (11) \AA , forming a figure-of-eight-shaped molecule, with each silver ion being coordinated by two pyridine N atoms. The silver ions are each further coordinated by the carboxamide O atom, O1, of neighbouring molecules, hence forming a three-dimensional

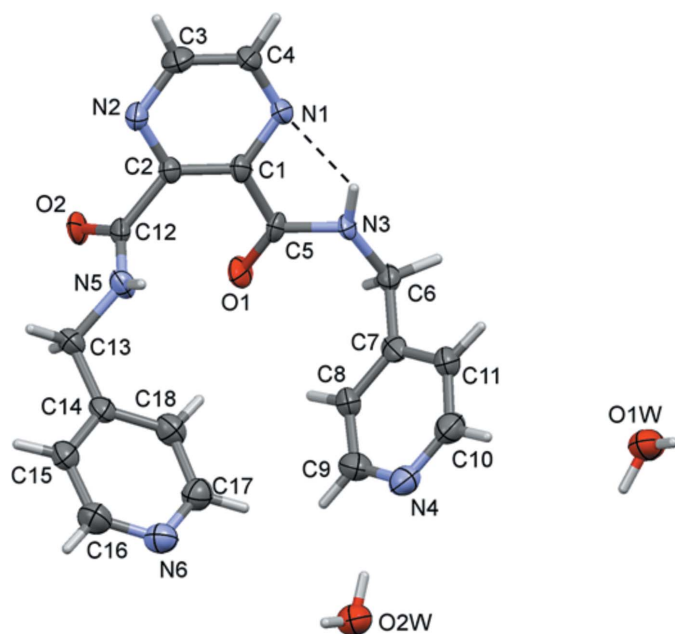


Figure 1
A view of the molecular structure of ligand (**L1**), with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular N—H...N contact is shown as a dashed line (see Table 2).

framework, illustrated in Fig. 3. If one considers that the silver ion, Ag1, is fivefold coordinate ($N_2O_2Ag^I$) then its coordination sphere can be described as distorted trigonal-bipyramidal, with a τ_5 value of 0.8 ($\tau_5 = 1$ for perfect trigonal-pyramidal geometry and 0 for perfect square-pyramidal geometry; Addison *et al.*, 1984). However, if one considers the Ag1 ion to be fourfold coordinate, N_2O_2 , with a τ_4 value of 0.55, its coordination sphere can be described as intermediate between trigonal-pyramidal and seesaw ($\tau_4 = 1$ for a perfect tetrahedral geometry and 0 for a perfect square-planar geometry. For intermediate structures, including trigonal-pyramidal and seesaw, τ_4 falls within the range of 0 to 1; Yang *et al.*, 2007). The nitrate anion that does not coordinate to the silver(I) ion is positionally disordered, and also located about a twofold rotation axis.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$) for (**L1**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-H3N\cdots N1$	0.88 (3)	2.08 (5)	2.718 (7)	129 (5)
$N5-H5N\cdots O1^i$	0.88 (3)	2.05 (4)	2.858 (7)	151 (6)
$O1W-H1WA\cdots O2W^{ii}$	0.86	1.91	2.762 (7)	177
$O1W-H1WB\cdots N6^{iii}$	0.94	1.97	2.886 (7)	164
$O2W-H2WA\cdots O1W^{iv}$	0.86	1.91	2.765 (8)	172
$O2W-H2WB\cdots N4$	0.85	2.06	2.888 (7)	164
$C3-H3\cdots O1W^v$	0.95	2.38	3.273 (8)	156
$C4-H4\cdots O2W^{vi}$	0.95	2.58	3.253 (8)	128
$C6-H6A\cdots N2^{vii}$	0.99	2.57	3.515 (8)	159
$C16-H16\cdots N4^{iv}$	0.95	2.60	3.451 (9)	149

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

Table 2
Selected geometric parameters (\AA , $^\circ$) for (**I**).

$Ag1-Ag1^i$	3.1638 (11)	$Ag1-O1^{ii}$	2.814 (5)
$Ag1-N4$	2.109 (5)		
$N4-Ag1-N4^{iii}$	173.0 (2)	$O1^{ii}-Ag1-N4$	97.80 (15)
$O1^{ii}-Ag1-O1^{iv}$	109.48 (14)	$O1^{iv}-Ag1-N4$	86.26 (15)
$Ag1^i-Ag1-N4$	86.51 (14)	$Ag1^i-Ag1-O1^{ii}$	125.26 (10)

Symmetry codes: (i) $x, -y+\frac{7}{4}, -z+\frac{3}{4}$; (ii) $x-\frac{1}{4}, y+\frac{1}{4}, -z+\frac{1}{2}$; (iii) $-x+\frac{7}{4}, y, -z+\frac{3}{4}$; (iv) $-x+2, y+\frac{1}{4}, z+\frac{1}{4}$.

3. Supramolecular features

In the crystal of ligand (**L1**), molecules are linked by N—H...O(water) hydrogen bonds forming chains propagating along the c -axis direction (Table 1 and Fig. 4). Parallel to this chain of molecules is a chain of hydrogen-bonded water molecules (Table 1 and Fig. 4), which is linked to the chain of (**L1**) molecules by O—H...N hydrogen bonds, forming columns propagating along the c axis. The columns are linked by C—H...O and C—H...N hydrogen bonds, forming a three-dimensional supramolecular structure (Table 1 and Fig. 5).

In (**I**), the nitrate anion is situated in the cavities of the three-dimensional framework and is linked to the framework by N—H...O and C—H...O hydrogen bonds (Table 3 and

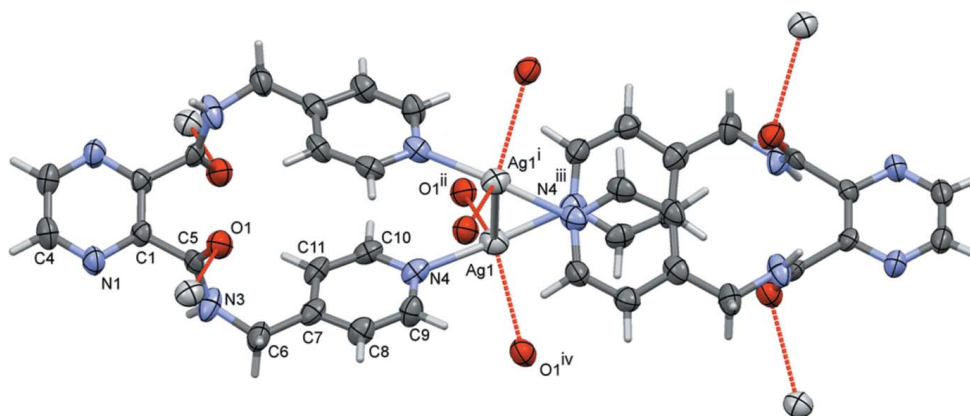


Figure 2
A view of the figure-eight arrangement of the title complex (**I**), with atom labelling for the asymmetric unit and some symmetry-related atoms (see Table 1 for details). The unlabelled atoms of the ligand on the left-hand-side of the figure are related to the labelled atoms by twofold rotational symmetry (symmetry operation: $-x+\frac{7}{4}, -y+\frac{7}{4}, z$). The nitrate anions have been omitted for clarity.

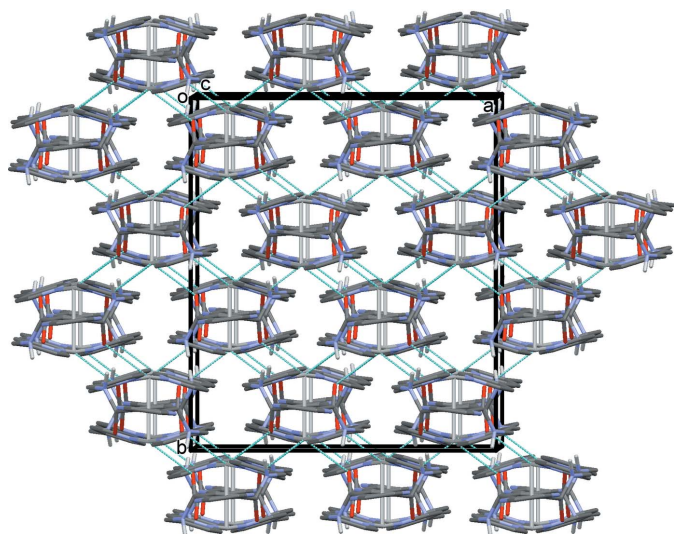


Figure 3
A view along the c axis of the three-dimensional framework of complex (**I**), showing the $\text{Ag}\cdots\text{O}$ bonds as dashed lines (see Table 2). The nitrate anions and the C-bound H atoms have been omitted for clarity.

Fig. 6). The nitrate anion in (**I**) is not essential for forming the three-dimensional structure, although it may act as a template for the formation of the framework (Batten *et al.*, 2009). This is in contrast to the MOF *catena*-[bis(μ_3 -nitrate- O,O',O'')-bis(μ_3 -1,3,5-tris(pyrazol-1-yl)benzene- N,N',N'')trisilver(I) nitrate] mentioned above (Shu *et al.*, 2006), in which there are nitrate anions coordinating the silver ions in a μ_3 fashion and present also in the framework cavities. There are, of course, other examples reported in the Cambridge Structural Database (Groom *et al.*, 2016).

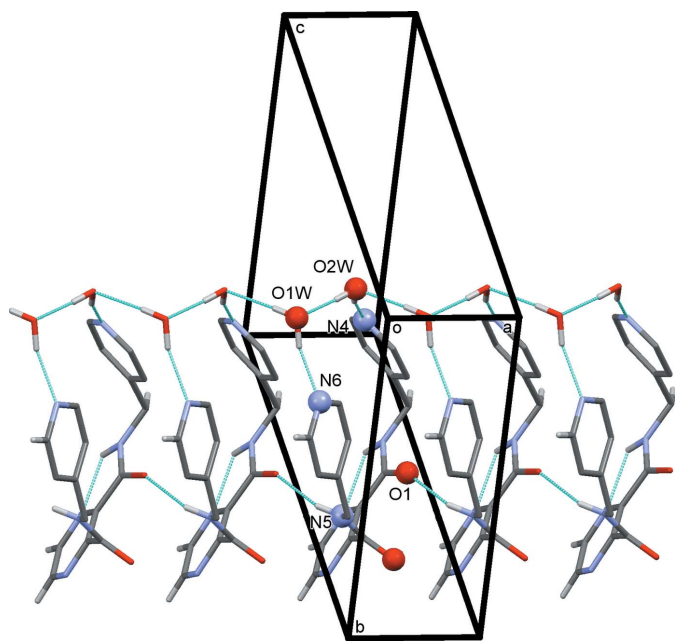


Figure 4
A partial view along direction [111] of the crystal packing of ligand (**L1**). The hydrogen bonds are shown as dashed lines (see Table 1)

Table 3
Hydrogen-bond geometry (\AA , $^\circ$) for (**I**).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3N}\cdots\text{O11}^{\text{v}}$	0.88	1.86	2.744 (14)	178
$\text{N3}-\text{H3N}\cdots\text{O13}^{\text{v}}$	0.88	2.26	2.875 (13)	127
$\text{C4}-\text{H4}\cdots\text{O11}^{\text{vi}}$	0.95	2.45	3.378 (13)	165
$\text{C4}-\text{H4}\cdots\text{O14}^{\text{vii}}$	0.95	2.40	3.33 (2)	168
$\text{C9}-\text{H9}\cdots\text{O13}^{\text{viii}}$	0.95	2.50	3.224 (14)	133
$\text{C11}-\text{H11}\cdots\text{O13}^{\text{v}}$	0.95	2.51	3.154 (13)	126

Symmetry codes: (v) $x, y + 1, z$; (vi) $-x + 2, -y + 1, -z$; (vii) $-x + 2, y + \frac{3}{2}, z - \frac{1}{2}$; (viii) $x + \frac{1}{2}, y + \frac{3}{2}, -z + \frac{1}{2}$.

In describing compound (**I**) as a three-dimensional coordination polymer, we make here the distinction between a coordination polymer and a metal–organic framework. Both have a three-dimensional framework but there are no cavities, even small ones, in the structure of (**I**). Hence, it should be classed as a three-dimensional coordination polymer according to the IUPAC recommendations on the ‘Terminology of metal–organic frameworks and coordination polymers’ (Batten *et al.*, 2013).

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update February 2017; Groom *et al.*, 2016) for Ag–Ag complexes, excluding silver ion clusters of any kind, gave 321 hits. Limiting the search to Ag–Ag complexes with each silver ion coordinated by two pyridine N atoms, gave 95 hits. The Ag–Ag distances vary between *ca* 2.6–3.6 \AA . One compound, bis[μ_2 -2,7-di-*tert*-butyl-9,9-dimethyl- N,N' -bis[(3-pyridyl)methyl]xanthene-4,5-dicarboxamide]disilver bis(trifluoromethanesulfonate) chloroform solvate (HIFKUD; Yue *et al.*, 2007), is particularly interesting because it too involves a

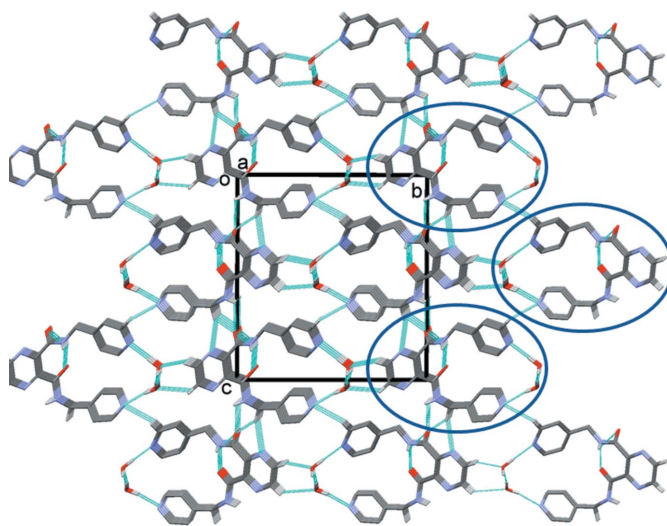
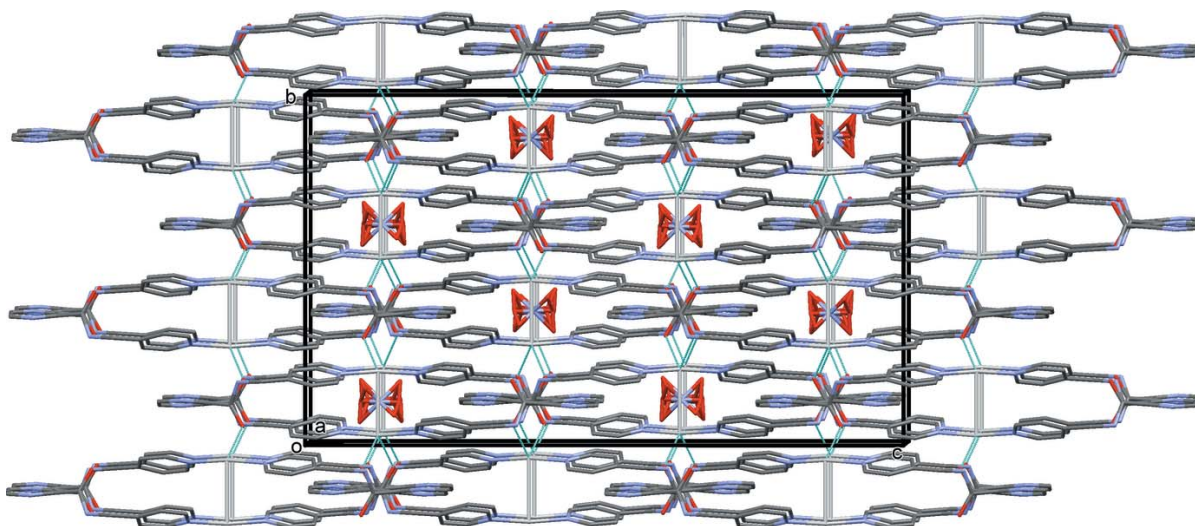


Figure 5
A view along the a axis of the crystal packing of ligand (**L1**). The columns of (**L1**) molecules, linked by hydrogen bonds involving the water molecules, are indicated by blue circles. The hydrogen bonds are shown as dashed lines (see Table 1), and for clarity, only the H atoms involved in hydrogen bonding have been included.


Figure 6

A view along the *a* axis of the crystal packing of complex (**I**), showing the Ag...O bonds as dashed lines (see Table 2). For clarity, all H atoms have been omitted.

dicarboxamide ligand, *viz.* *N,N'*-bis[(3-pyridyl)methyl]xanthene-4,5-dicarboxamide), that wraps around an Ag–Ag bond forming a similar figure-of-eight-shaped complex. Here the Ag–Ag bond length is 3.134 (1) Å, slightly shorter than the value of 3.1638 (11) Å observed in (**I**); Table 2. A search for the benzene analogue of ligand (**L1**), *N*-(4-pyridylmethyl)-carbamoylbenzene, gave only two hits. Both of them are mercury(II) complexes, *viz.* the binuclear complex bis[μ_2 -1,2-bis[*N*-(4-pyridylmethyl)carbamoyl]benzene]tetrakis(trifluoroacetato)dimercury(II) methanol solvate (XAHSIJ; Burchell *et al.*, 2004) and the two-dimensional network *catena*-[bis[μ_2 -1,2-bis[*N*-(4-pyridylmethyl)carbamoyl]benzene]dichlorido-mercury(II) 1,2-dichloroethane solvate] (XAHSOP; Burchell *et al.*, 2004). A search for the benzene analogue of ligand (**L2**), [*N*-(2-pyridylmethyl)carbamoyl]benzene, gave zero hits, while that for [*N*-(3-pyridylmethyl)carbamoyl]benzene gave eight hits. The latter includes the crystal structure of the dihydrate of the ligand itself (PANROM; Ge *et al.*, 2005) and the structures of seven first-row transition metal one-, two- and three-dimensional coordination polymers.

5. Synthesis and crystallization

Ligand (**L1**) was prepared using the same procedure as for ligand (**L2**) (Cati *et al.*, 2004). Dimethyl pyrazine-2,3-dicarboxylate (1.96 g, 10 mmol; Alvarez-Ibarra *et al.*, 1994) and an excess of 4-(aminomethyl)pyridine (3.24 g, 30 mmol) in 35 ml of methanol were heated to reflux and heating was continued for 72 h in a two-necked flask (100 ml). The brown solution that formed was concentrated and 15 ml of water were added, which precipitated quantitatively ligand (**L1**). The solid was collected by filtration, washed with 10 ml of water and dried in air. Recrystallization in ethanol gave colourless plate-like crystals (yield is quantitative; m.p. 474 K). Spectroscopic data: ¹H NMR (400 MHz, DMSO-*d*₆): 9.33 (*t*, 1H,

$J_{\text{hg}} = 6.1$, Hh); 8.86 (*s*, 1H, Hn = Hm); 8.49 (*dd*, 2H, $J_{\text{ba}} = 4.5$, $J_{\text{be}} = 1.5$, Hb = Hd); 7.39 (*dd*, 2H, $J_{\text{ab}} = 4.5$, $J_{\text{eb}} = 1.5$, Ha = He); 4.52 (*d*, 2H, $J_{\text{gh}} = 6.1$, Hg). ¹³C NMR (400 MHz, DMSO-*d*₆): 165.8, 150.3, 148.9, 147.6, 145.6, 123.0, 42.2. IR (KBr pellet, cm⁻¹): 3273 (*s*), 3031 (*s*), 1675 (*vs*), 1602 (*vs*), 1564 (*vs*), 1520 (*vs*), 1416 (*vs*), 1364 (*s*), 1311 (*s*), 1292 (*s*), 1220 (*s*), 1185 (*m*), 1164 (*m*), 1124 (*s*), 1069 (*m*), 995 (*s*), 871 (*w*), 830 (*m*), 787 (*m*), 745 (*m*), 715 (*m*), 611 (*m*), 575 (*w*), 504 (*m*), 495 (*m*), 475 (*m*). Elemental analysis for [C₁₈H₁₆N₆O₂]·H₂O ($M_r = 366.39$ g mol⁻¹): calculated: C: 59.01 H: 4.95 N: 22.94%; found: C: 59.10 H: 5.05 N: 23.10%.

Complex (**I**): A solution of (**L1**) (46 mg; 0.126 mmol) in 6 ml CHCl₃ was introduced into a 13 mm diameter glass tube. It was layered with methanol (*ca* 2 ml) used as a buffer zone. A solution of AgNO₃ (21 mg, 0.126 mmol) in MeOH (6 ml) was then added gently to avoid possible mixing. The glass tube was sealed with a perforated parafilm and left at room temperature. Colourless block-like crystals were obtained after a few days (yield 60 mg, 92%). Elemental analysis for AgC₁₈H₁₆N₆O₅: ($M_r = 518.25$ g mol⁻¹): calculated: C: 41.72 H: 3.11 N: 18.92%; found: C: 41.65 H: 3.09 N: 18.85%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. For the ligand (**L1**), the NH and water H atoms were located in difference-Fourier maps and refined with distance restraints: O–H = 0.85 (2) Å, N–H = 0.88 (2) Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ and $1.2U_{\text{eq}}(\text{N})$. In the final cycles of refinement, the water H atoms were treated as riding atoms. For complex (**I**), the NH H atoms were included in calculated positions and treated as riding: N–H = 0.88 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. For both compounds, the C-bound H atoms were included in calculated positions and refined as riding: C–H = 0.95–0.99 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The

Table 4
Experimental details.

	(L1)	(I)
Crystal data		
Chemical formula	C ₁₈ H ₁₆ N ₆ O ₂ ·2H ₂ O	[Ag(C ₁₈ H ₁₆ N ₆ O ₂)]NO ₃
<i>M_r</i>	384.40	518.25
Crystal system, space group	Monoclinic, <i>Pc</i>	Orthorhombic, <i>Fddd</i>
Temperature (K)	153	153
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.3677 (6), 14.0232 (12), 15.1816 (18)	14.9776 (16), 17.3228 (12), 29.570 (4)
α , β , γ (°)	90, 96.153 (16), 90	90, 90, 90
<i>V</i> (Å ³)	924.50 (19)	7672.1 (14)
<i>Z</i>	2	16
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.10	1.10
Crystal size (mm)	0.50 × 0.15 × 0.05	0.40 × 0.30 × 0.20
Data collection		
Diffractometer	Stoe IPDS 1	Stoe IPDS 1
Absorption correction	Multi-scan (<i>MULABS</i> ; Spek, 2009)	Multi-scan (<i>MULABS</i> ; Spek, 2009)
<i>T</i> _{min} , <i>T</i> _{max}	0.763, 1.000	0.985, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7134, 3388, 1693	13548, 1721, 1038
<i>R</i> _{int}	0.107	0.096
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.615	0.600
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.051, 0.122, 0.77	0.045, 0.107, 0.90
No. of reflections	3388	1721
No. of parameters	260	141
No. of restraints	8	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.21, -0.25	0.68, -0.65

Computer programs: *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004), *SHELXS2014* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

nitrate anion is positionally disordered about a twofold rotation axis and was refined with fixed occupancies (N10A and N10B = 0.5, O11 and O13 = 0.5, O12 and O14 = 0.25), and all their ADP's were made equal to that of atom O11. Using a one-circle image-plate diffraction system it is not possible to measure 100% of the Ewald sphere, particularly for triclinic or monoclinic systems. This is the case for ligand (L1), which crystallized in the monoclinic space group *Pc* and for which only 94.7% of the Ewald sphere was accessible.

Funding information

Funding for this research was provided by: Swiss National Science Foundation; University of Neuchâtel.

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supporting information

Acta Cryst. (2017). E73, 798-803 [https://doi.org/10.1107/S2056989017006387]

Crystal structure of a pyrazine-2,3-dicarboxamide ligand and of its silver(I) nitrate complex, a three-dimensional coordination polymer

Dilovan S. Cati and Helen Stoeckli-Evans

Computing details

For both compounds, data collection: *EXPOSE* in *IPDS-I* (Stoe & Cie, 2004); cell refinement: *CELL* in *IPDS-I* (Stoe & Cie, 2004); data reduction: *INTEGRATE* in *IPDS-I* (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

(L1) *N*²,*N*³-Bis(pyridin-4-ylmethyl)pyrazine-2,3-dicarboxamide

Crystal data

C₁₈H₁₆N₆O₂·2H₂O

M_r = 384.40

Monoclinic, *Pc*

a = 4.3677 (6) Å

b = 14.0232 (12) Å

c = 15.1816 (18) Å

β = 96.153 (16)°

V = 924.50 (19) Å³

Z = 2

F(000) = 404

D_x = 1.381 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 3264 reflections

θ = 2.0–25.9°

μ = 0.10 mm⁻¹

T = 153 K

Plate, colourless

0.50 × 0.15 × 0.05 mm

Data collection

Stoe IPDS 1

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

φ rotation scans

Absorption correction: multi-scan

(MULABS; Spek, 2009)

T_{min} = 0.763, *T_{max}* = 1.000

7134 measured reflections

3388 independent reflections

1693 reflections with *I* > 2σ(*I*)

R_{int} = 0.107

θ_{max} = 25.9°, θ_{min} = 2.0°

h = -5→5

k = -17→16

l = -18→18

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.051

wR(*F*²) = 0.122

S = 0.77

3388 reflections

260 parameters

8 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0453*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

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

$$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$$

Extinction correction: (SHELXL2016;
Sheldrick, 2015),
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.036 (6)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7750 (11)	0.9108 (3)	0.4491 (3)	0.0358 (13)
O2	0.5478 (11)	0.9994 (3)	0.2578 (3)	0.0351 (12)
N1	0.4263 (14)	1.1135 (3)	0.5363 (4)	0.0321 (15)
N2	0.1716 (14)	1.1331 (4)	0.3588 (4)	0.0330 (15)
N3	0.7147 (13)	0.9491 (3)	0.5921 (3)	0.0258 (14)
H3N	0.612 (13)	0.998 (3)	0.609 (4)	0.031*
N4	0.4923 (14)	0.5966 (4)	0.6225 (4)	0.0403 (16)
N5	0.1699 (14)	0.9119 (4)	0.3107 (4)	0.0313 (14)
H5N	0.002 (11)	0.906 (5)	0.337 (4)	0.038*
N6	-0.0999 (16)	0.5615 (4)	0.3180 (4)	0.0436 (17)
C1	0.4668 (15)	1.0457 (4)	0.4743 (4)	0.0267 (17)
C2	0.3401 (16)	1.0564 (4)	0.3878 (4)	0.0258 (16)
C3	0.1396 (19)	1.1999 (5)	0.4209 (5)	0.043 (2)
H3	0.030625	1.256737	0.403978	0.051*
C4	0.2586 (18)	1.1888 (4)	0.5079 (5)	0.0360 (19)
H4	0.219526	1.236935	0.549295	0.043*
C5	0.6613 (15)	0.9624 (4)	0.5039 (4)	0.0280 (16)
C6	0.9192 (16)	0.8748 (4)	0.6312 (5)	0.0290 (17)
H6A	0.985533	0.891453	0.693707	0.035*
H6B	1.105193	0.872221	0.599314	0.035*
C7	0.7688 (16)	0.7778 (4)	0.6278 (5)	0.0307 (17)
C8	0.8016 (18)	0.7151 (4)	0.5602 (5)	0.0376 (19)
H8	0.917205	0.733033	0.513344	0.045*
C9	0.669 (2)	0.6270 (5)	0.5600 (5)	0.046 (2)
H9	0.702062	0.584555	0.513239	0.056*
C10	0.4698 (19)	0.6573 (5)	0.6889 (5)	0.044 (2)
H10	0.357252	0.636975	0.735668	0.053*
C11	0.5967 (17)	0.7473 (5)	0.6950 (5)	0.0374 (19)
H11	0.568042	0.787610	0.743743	0.045*
C12	0.3639 (17)	0.9848 (4)	0.3138 (4)	0.0297 (17)
C13	0.1367 (17)	0.8444 (4)	0.2372 (5)	0.0337 (18)
H13A	0.332934	0.841179	0.210178	0.040*
H13B	-0.024426	0.867753	0.191430	0.040*
C14	0.0529 (17)	0.7469 (4)	0.2655 (4)	0.0303 (17)
C15	-0.1501 (17)	0.6908 (5)	0.2141 (5)	0.0362 (18)

H15	-0.242090	0.714271	0.158778	0.043*
C16	-0.224 (2)	0.6001 (5)	0.2413 (5)	0.049 (2)
H16	-0.368187	0.563552	0.204091	0.058*
C17	0.1048 (19)	0.6151 (5)	0.3680 (6)	0.042 (2)
H17	0.200289	0.589113	0.421904	0.050*
C18	0.1843 (19)	0.7075 (5)	0.3446 (5)	0.0389 (18)
H18	0.327922	0.743333	0.382699	0.047*
O1W	0.7645 (12)	0.5986 (3)	0.9268 (3)	0.0503 (15)
H1WA	0.624209	0.595327	0.962023	0.075*
H1WB	0.768245	0.545186	0.889768	0.075*
O2W	0.3065 (12)	0.4183 (3)	0.5379 (3)	0.0478 (14)
H2WA	0.133161	0.418283	0.504471	0.072*
H2WB	0.327355	0.474826	0.557396	0.072*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.051 (3)	0.039 (3)	0.021 (3)	0.009 (2)	0.019 (3)	0.000 (2)
O2	0.052 (3)	0.040 (2)	0.015 (3)	-0.005 (2)	0.015 (2)	-0.0003 (19)
N1	0.055 (4)	0.024 (3)	0.018 (3)	0.001 (3)	0.007 (3)	-0.002 (2)
N2	0.050 (4)	0.030 (3)	0.019 (3)	0.006 (3)	0.004 (3)	0.003 (2)
N3	0.041 (4)	0.025 (3)	0.012 (3)	0.004 (3)	0.009 (3)	-0.001 (2)
N4	0.047 (4)	0.032 (3)	0.041 (4)	0.001 (3)	0.001 (4)	0.007 (3)
N5	0.038 (4)	0.034 (3)	0.023 (3)	-0.010 (3)	0.006 (3)	-0.006 (2)
N6	0.054 (4)	0.033 (3)	0.044 (4)	-0.005 (3)	0.007 (4)	-0.003 (3)
C1	0.035 (5)	0.029 (3)	0.018 (4)	-0.002 (3)	0.009 (3)	0.001 (3)
C2	0.034 (4)	0.025 (3)	0.020 (4)	0.000 (3)	0.008 (3)	0.000 (3)
C3	0.061 (6)	0.027 (4)	0.040 (5)	0.011 (4)	0.003 (4)	0.003 (3)
C4	0.060 (5)	0.025 (4)	0.023 (4)	0.007 (4)	0.009 (4)	-0.003 (3)
C5	0.037 (4)	0.031 (4)	0.017 (4)	-0.001 (3)	0.006 (3)	0.008 (3)
C6	0.036 (4)	0.031 (4)	0.020 (4)	0.006 (3)	0.001 (3)	0.000 (3)
C7	0.032 (5)	0.030 (4)	0.027 (4)	0.013 (3)	-0.007 (4)	-0.002 (3)
C8	0.056 (5)	0.034 (4)	0.022 (5)	0.001 (4)	0.001 (4)	-0.001 (3)
C9	0.066 (6)	0.031 (4)	0.040 (5)	0.005 (4)	0.001 (5)	-0.005 (3)
C10	0.057 (6)	0.037 (4)	0.039 (5)	0.007 (4)	0.009 (4)	0.007 (4)
C11	0.053 (5)	0.035 (4)	0.024 (4)	0.002 (4)	0.006 (4)	-0.001 (3)
C12	0.047 (5)	0.027 (4)	0.015 (4)	0.007 (3)	-0.002 (4)	0.001 (3)
C13	0.047 (5)	0.029 (3)	0.025 (4)	-0.003 (3)	0.003 (4)	-0.007 (3)
C14	0.038 (5)	0.029 (3)	0.025 (5)	0.005 (3)	0.006 (4)	-0.005 (3)
C15	0.047 (5)	0.035 (4)	0.028 (4)	0.005 (4)	0.007 (4)	-0.003 (3)
C16	0.063 (6)	0.040 (4)	0.042 (5)	-0.008 (4)	0.000 (5)	-0.004 (4)
C17	0.052 (5)	0.038 (4)	0.038 (5)	0.001 (4)	0.012 (4)	0.003 (4)
C18	0.041 (5)	0.040 (4)	0.036 (5)	-0.003 (4)	0.002 (4)	-0.006 (3)
O1W	0.066 (4)	0.036 (3)	0.051 (4)	-0.006 (3)	0.013 (3)	-0.001 (2)
O2W	0.061 (4)	0.036 (3)	0.047 (3)	0.000 (2)	0.007 (3)	0.001 (2)

Geometric parameters (Å, °)

O1—C5	1.245 (7)	C6—H6B	0.9900
O2—C12	1.248 (7)	C7—C8	1.370 (9)
N1—C4	1.331 (8)	C7—C11	1.398 (9)
N1—C1	1.364 (8)	C8—C9	1.364 (10)
N2—C3	1.346 (9)	C8—H8	0.9500
N2—C2	1.351 (8)	C9—H9	0.9500
N3—C5	1.347 (8)	C10—C11	1.378 (10)
N3—C6	1.456 (8)	C10—H10	0.9500
N3—H3N	0.88 (3)	C11—H11	0.9500
N4—C10	1.330 (9)	C13—C14	1.491 (8)
N4—C9	1.354 (10)	C13—H13A	0.9900
N5—C12	1.325 (8)	C13—H13B	0.9900
N5—C13	1.458 (8)	C14—C15	1.366 (10)
N5—H5N	0.88 (3)	C14—C18	1.389 (10)
N6—C17	1.340 (10)	C15—C16	1.386 (9)
N6—C16	1.344 (10)	C15—H15	0.9500
C1—C2	1.377 (9)	C16—H16	0.9500
C1—C5	1.485 (8)	C17—C18	1.397 (10)
C2—C12	1.518 (9)	C17—H17	0.9500
C3—C4	1.375 (10)	C18—H18	0.9500
C3—H3	0.9500	O1W—H1WA	0.8569
C4—H4	0.9500	O1W—H1WB	0.9371
C6—C7	1.510 (9)	O2W—H2WA	0.8649
C6—H6A	0.9900	O2W—H2WB	0.8483
C4—N1—C1	115.9 (6)	C7—C8—H8	119.9
C3—N2—C2	114.8 (6)	N4—C9—C8	123.9 (7)
C5—N3—C6	122.5 (5)	N4—C9—H9	118.1
C5—N3—H3N	99 (4)	C8—C9—H9	118.1
C6—N3—H3N	139 (5)	N4—C10—C11	125.2 (7)
C10—N4—C9	115.0 (6)	N4—C10—H10	117.4
C12—N5—C13	122.6 (6)	C11—C10—H10	117.4
C12—N5—H5N	128 (4)	C10—C11—C7	118.3 (6)
C13—N5—H5N	106 (4)	C10—C11—H11	120.8
C17—N6—C16	116.6 (6)	C7—C11—H11	120.8
N1—C1—C2	120.9 (6)	O2—C12—N5	123.9 (6)
N1—C1—C5	116.8 (6)	O2—C12—C2	119.7 (6)
C2—C1—C5	122.2 (5)	N5—C12—C2	116.2 (6)
N2—C2—C1	123.1 (5)	N5—C13—C14	112.5 (6)
N2—C2—C12	111.4 (6)	N5—C13—H13A	109.1
C1—C2—C12	125.5 (6)	C14—C13—H13A	109.1
N2—C3—C4	122.5 (7)	N5—C13—H13B	109.1
N2—C3—H3	118.7	C14—C13—H13B	109.1
C4—C3—H3	118.7	H13A—C13—H13B	107.8
N1—C4—C3	122.6 (6)	C15—C14—C18	116.6 (6)
N1—C4—H4	118.7	C15—C14—C13	121.9 (6)

C3—C4—H4	118.7	C18—C14—C13	121.5 (6)
O1—C5—N3	123.0 (6)	C14—C15—C16	121.0 (7)
O1—C5—C1	120.7 (6)	C14—C15—H15	119.5
N3—C5—C1	116.3 (5)	C16—C15—H15	119.5
N3—C6—C7	112.7 (6)	N6—C16—C15	122.9 (7)
N3—C6—H6A	109.1	N6—C16—H16	118.6
C7—C6—H6A	109.1	C15—C16—H16	118.6
N3—C6—H6B	109.1	N6—C17—C18	123.0 (8)
C7—C6—H6B	109.1	N6—C17—H17	118.5
H6A—C6—H6B	107.8	C18—C17—H17	118.5
C8—C7—C11	117.3 (6)	C14—C18—C17	119.9 (7)
C8—C7—C6	121.6 (6)	C14—C18—H18	120.1
C11—C7—C6	121.1 (6)	C17—C18—H18	120.1
C9—C8—C7	120.3 (7)	H1WA—O1W—H1WB	113.1
C9—C8—H8	119.9	H2WA—O2W—H2WB	105.0
C4—N1—C1—C2	0.2 (9)	C7—C8—C9—N4	2.1 (12)
C4—N1—C1—C5	178.1 (6)	C9—N4—C10—C11	3.4 (12)
C3—N2—C2—C1	0.9 (10)	N4—C10—C11—C7	-1.4 (12)
C3—N2—C2—C12	179.9 (6)	C8—C7—C11—C10	-0.5 (11)
N1—C1—C2—N2	0.3 (10)	C6—C7—C11—C10	-178.9 (6)
C5—C1—C2—N2	-177.6 (6)	C13—N5—C12—O2	-4.5 (10)
N1—C1—C2—C12	-178.5 (6)	C13—N5—C12—C2	171.7 (6)
C5—C1—C2—C12	3.6 (10)	N2—C2—C12—O2	78.2 (8)
C2—N2—C3—C4	-2.5 (11)	C1—C2—C12—O2	-102.8 (8)
C1—N1—C4—C3	-1.8 (10)	N2—C2—C12—N5	-98.1 (7)
N2—C3—C4—N1	3.2 (12)	C1—C2—C12—N5	80.8 (9)
C6—N3—C5—O1	2.1 (10)	C12—N5—C13—C14	148.9 (6)
C6—N3—C5—C1	-175.4 (5)	N5—C13—C14—C15	141.5 (7)
N1—C1—C5—O1	-161.3 (6)	N5—C13—C14—C18	-40.3 (9)
C2—C1—C5—O1	16.6 (9)	C18—C14—C15—C16	1.4 (10)
N1—C1—C5—N3	16.2 (8)	C13—C14—C15—C16	179.6 (6)
C2—C1—C5—N3	-165.8 (6)	C17—N6—C16—C15	-0.6 (11)
C5—N3—C6—C7	-79.3 (7)	C14—C15—C16—N6	-0.9 (12)
N3—C6—C7—C8	94.4 (7)	C16—N6—C17—C18	1.6 (11)
N3—C6—C7—C11	-87.3 (8)	C15—C14—C18—C17	-0.4 (10)
C11—C7—C8—C9	0.1 (11)	C13—C14—C18—C17	-178.7 (6)
C6—C7—C8—C9	178.5 (7)	N6—C17—C18—C14	-1.2 (11)
C10—N4—C9—C8	-3.8 (11)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3N \cdots N1	0.88 (3)	2.08 (5)	2.718 (7)	129 (5)
N5—H5N \cdots O1 ⁱ	0.88 (3)	2.05 (4)	2.858 (7)	151 (6)
O1W—H1WA \cdots O2W ⁱⁱ	0.86	1.91	2.762 (7)	177
O1W—H1WB \cdots N6 ⁱⁱⁱ	0.94	1.97	2.886 (7)	164
O2W—H2WA \cdots O1W ^{iv}	0.86	1.91	2.765 (8)	172

O2W—H2WB··N4	0.85	2.06	2.888 (7)	164
C3—H3··O1W ^v	0.95	2.38	3.273 (8)	156
C4—H4··O2W ^{vi}	0.95	2.58	3.253 (8)	128
C6—H6A··N2 ^{vii}	0.99	2.57	3.515 (8)	159
C16—H16··N4 ^{iv}	0.95	2.60	3.451 (9)	149

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

(I) Poly[[[μ_4 - N^2, N^3 -bis(pyridin-4-ylmethyl)pyrazine-2,3-dicarboxamide]silver(I)] nitrate]

Crystal data

[Ag(C₁₈H₁₆N₆O₂)]NO₃

$M_r = 518.25$

Orthorhombic, *Fddd*

$a = 14.9776$ (16) Å

$b = 17.3228$ (12) Å

$c = 29.570$ (4) Å

$V = 7672.1$ (14) Å³

$Z = 16$

$F(000) = 4160$

$D_x = 1.795$ Mg m⁻³

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

Cell parameters from 6115 reflections

$\theta = 1.9$ – 25.9°

$\mu = 1.10$ mm⁻¹

$T = 153$ K

Block, colourless

$0.40 \times 0.30 \times 0.20$ mm

Data collection

Stoe IPDS 1

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

φ rotation scans

Absorption correction: multi-scan

(MULABS; Spek, 2009)

$T_{\min} = 0.985$, $T_{\max} = 1.000$

13548 measured reflections

1721 independent reflections

1038 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.096$

$\theta_{\max} = 25.3^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -17 \rightarrow 17$

$k = -20 \rightarrow 20$

$l = -35 \rightarrow 35$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.107$

$S = 0.90$

1721 reflections

141 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$

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

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.68$ e Å⁻³

$\Delta\rho_{\min} = -0.65$ e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ag1	0.87500	0.96632 (4)	0.37500	0.0464 (2)	
O1	0.9796 (3)	0.8101 (3)	0.14979 (13)	0.0483 (14)	
N1	0.9673 (3)	0.8836 (3)	0.04722 (14)	0.0447 (18)	

N3	1.0135 (3)	0.9361 (3)	0.14261 (16)	0.050 (2)	
N4	0.9359 (3)	0.9589 (3)	0.31086 (16)	0.0427 (17)	
C1	0.9207 (3)	0.8777 (4)	0.08584 (15)	0.0337 (16)	
C4	0.9204 (4)	0.8805 (4)	0.00937 (17)	0.0453 (19)	
C5	0.9745 (3)	0.8715 (4)	0.12935 (16)	0.0340 (18)	
C6	1.0689 (4)	0.9393 (4)	0.18277 (18)	0.051 (2)	
C7	1.0197 (4)	0.9446 (3)	0.22692 (19)	0.0437 (19)	
C8	1.0640 (4)	0.9276 (4)	0.26675 (19)	0.045 (2)	
C9	1.0221 (4)	0.9354 (4)	0.3075 (2)	0.046 (2)	
C10	0.8921 (3)	0.9745 (3)	0.27201 (19)	0.043 (2)	
C11	0.9302 (4)	0.9686 (4)	0.23033 (19)	0.0447 (19)	
O11	0.9918 (8)	0.0666 (8)	0.0912 (4)	0.089 (3)	0.500
O12	1.0655 (16)	0.1323 (15)	0.1063 (6)	0.089 (3)	0.250
O13	0.9326 (9)	0.0862 (7)	0.1489 (4)	0.089 (3)	0.500
O14	0.9869 (18)	0.1233 (19)	0.1570 (7)	0.089 (3)	0.250
N10A	0.9614 (15)	0.12500	0.12500	0.089 (3)	0.500
N10B	0.9960 (16)	0.12500	0.12500	0.089 (3)	0.500
H4	0.95046	0.88600	-0.01873	0.0540*	
H3N	1.00563	0.97838	0.12661	0.0600*	
H6A	1.10904	0.98449	0.18023	0.0610*	
H6B	1.10697	0.89253	0.18345	0.0610*	
H8	1.12416	0.91024	0.26574	0.0540*	
H9	1.05428	0.92399	0.33436	0.0560*	
H10	0.83154	0.99047	0.27385	0.0520*	
H11	0.89687	0.98062	0.20392	0.0530*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0474 (4)	0.0397 (4)	0.0521 (4)	0.0000	0.0035 (4)	0.0000
O1	0.048 (2)	0.054 (3)	0.043 (2)	0.000 (2)	-0.005 (2)	0.010 (2)
N1	0.047 (3)	0.057 (4)	0.030 (2)	0.003 (3)	0.004 (2)	-0.004 (2)
N3	0.078 (4)	0.035 (4)	0.037 (3)	0.002 (3)	-0.015 (3)	-0.006 (2)
N4	0.042 (3)	0.039 (3)	0.047 (3)	0.001 (2)	-0.009 (2)	-0.006 (2)
C1	0.037 (2)	0.035 (3)	0.029 (3)	0.005 (3)	0.002 (2)	-0.010 (3)
C4	0.059 (3)	0.047 (4)	0.030 (3)	0.009 (4)	0.006 (2)	0.000 (3)
C5	0.030 (2)	0.046 (4)	0.026 (3)	0.005 (2)	0.010 (2)	-0.007 (4)
C6	0.062 (4)	0.057 (5)	0.033 (3)	-0.003 (3)	-0.008 (3)	-0.006 (3)
C7	0.051 (3)	0.036 (4)	0.044 (3)	-0.004 (3)	-0.012 (3)	-0.008 (3)
C8	0.046 (3)	0.044 (4)	0.045 (4)	0.007 (3)	-0.006 (3)	-0.004 (3)
C9	0.051 (4)	0.051 (4)	0.037 (3)	0.009 (3)	-0.008 (3)	0.000 (3)
C10	0.037 (4)	0.041 (4)	0.052 (3)	-0.004 (3)	-0.010 (3)	-0.006 (3)
C11	0.050 (3)	0.045 (4)	0.039 (3)	-0.001 (3)	-0.015 (3)	-0.008 (3)
O11	0.112 (6)	0.088 (6)	0.067 (4)	0.0000	0.0000	0.028 (4)
O12	0.112 (6)	0.088 (6)	0.067 (4)	0.0000	0.0000	0.028 (4)
O13	0.112 (6)	0.088 (6)	0.067 (4)	0.0000	0.0000	0.028 (4)
O14	0.112 (6)	0.088 (6)	0.067 (4)	0.0000	0.0000	0.028 (4)
N10A	0.112 (6)	0.088 (6)	0.067 (4)	0.0000	0.0000	0.028 (4)

N10B	0.112 (6)	0.088 (6)	0.067 (4)	0.0000	0.0000	0.028 (4)
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Geometric parameters (Å, °)

Ag1—Ag1 ⁱ	3.1638 (11)	C8—C9	1.365 (8)
Ag1—N4	2.109 (5)	C10—C11	1.362 (8)
Ag1—O1 ⁱⁱ	2.814 (5)	O11—N10A	1.493 (14)
Ag1—O1 ⁱⁱⁱ	2.814 (5)	O11—N10B	1.424 (13)
Ag1—N4 ^{iv}	2.109 (5)	O11—O12	1.65 (3)
O1—C5	1.226 (8)	O12—N10B	1.19 (3)
N1—C1	1.342 (6)	O12—N10A	1.66 (3)
N1—C4	1.323 (7)	O13—N10A	1.066 (15)
N3—C5	1.322 (8)	O13—N10B	1.36 (2)
N3—C6	1.450 (7)	O13—O14	1.06 (3)
N4—C9	1.357 (8)	O14—N10B	0.96 (2)
N4—C10	1.350 (7)	O14—N10A	1.02 (2)
C1—C5	1.522 (6)	C4—H4	0.9500
C1—C1 ^v	1.372 (6)	C6—H6B	0.9900
C4—C4 ^v	1.373 (9)	C6—H6A	0.9900
N3—H3N	0.8800	C8—H8	0.9500
C6—C7	1.502 (8)	C9—H9	0.9500
C7—C8	1.384 (8)	C10—H10	0.9500
C7—C11	1.407 (8)	C11—H11	0.9500
N4—Ag1—N4 ^{iv}	173.0 (2)	C6—C7—C8	119.5 (5)
O1 ⁱⁱ —Ag1—O1 ⁱⁱⁱ	109.48 (14)	C6—C7—C11	123.2 (5)
Ag1 ⁱ —Ag1—N4	86.51 (14)	C7—C8—C9	120.7 (6)
O1 ⁱⁱ —Ag1—N4	97.80 (15)	N4—C9—C8	122.1 (5)
O1 ⁱⁱⁱ —Ag1—N4	86.26 (15)	N4—C10—C11	123.5 (5)
Ag1 ⁱ —Ag1—O1 ⁱⁱ	125.26 (10)	C7—C11—C10	119.1 (5)
Ag1 ⁱ —Ag1—O1 ⁱⁱⁱ	125.26 (10)	C4 ^v —C4—H4	119.00
Ag1 ⁱ —Ag1—N4 ^{iv}	86.51 (14)	N1—C4—H4	119.00
O1 ⁱⁱ —Ag1—N4 ^{iv}	86.26 (15)	N3—C6—H6B	108.00
O1 ⁱⁱⁱ —Ag1—N4 ^{iv}	97.80 (15)	C7—C6—H6A	108.00
Ag1 ^{vi} —O1—C5	114.9 (3)	H6A—C6—H6B	107.00
C1—N1—C4	116.2 (5)	C7—C6—H6B	108.00
C5—N3—C6	121.9 (5)	N3—C6—H6A	108.00
Ag1—N4—C9	119.7 (4)	C7—C8—H8	120.00
Ag1—N4—C10	122.9 (3)	C9—C8—H8	120.00
C9—N4—C10	117.4 (5)	C8—C9—H9	119.00
N1—C1—C5	116.7 (4)	N4—C9—H9	119.00
N1—C1—C1 ^v	121.6 (4)	N4—C10—H10	118.00
C1 ^v —C1—C5	121.6 (4)	C11—C10—H10	118.00
N1—C4—C4 ^v	122.1 (5)	O11—N10A—O13	98.0 (8)
C5—N3—H3N	119.00	O13—N10A—N10B	113.9 (13)
C6—N3—H3N	119.00	O11—N10A—N10B	72.3 (9)
O1—C5—N3	124.1 (5)	O11—N10B—N10A	87.5 (11)
O1—C5—C1	120.7 (6)	O11—N10B—O13	89.0 (10)

N3—C5—C1	115.2 (5)	O13—N10B—N10A	45.8 (9)
N3—C6—C7	115.7 (5)	C7—C11—H11	120.00
C8—C7—C11	117.3 (5)	C10—C11—H11	120.00
Ag1 ⁱ —Ag1—N4—C9	-71.9 (5)	N1—C1—C5—O1	-106.9 (6)
Ag1 ⁱ —Ag1—N4—C10	106.2 (4)	N1—C1—C5—N3	73.3 (7)
O1 ⁱⁱ —Ag1—N4—C9	163.0 (5)	C1 ^v —C1—C5—O1	68.8 (8)
O1 ⁱⁱ —Ag1—N4—C10	-19.0 (5)	C1 ^v —C1—C5—N3	-111.0 (7)
O1 ⁱⁱⁱ —Ag1—N4—C9	53.8 (5)	N1—C1—C1 ^v —N1 ^v	5.5 (11)
O1 ⁱⁱⁱ —Ag1—N4—C10	-128.1 (5)	N1—C1—C1 ^v —C5 ^v	-170.1 (6)
Ag1 ^{vi} —O1—C5—N3	-89.1 (5)	C5—C1—C1 ^v —N1 ^v	-170.1 (6)
Ag1 ^{vi} —O1—C5—C1	91.1 (5)	C5—C1—C1 ^v —C5 ^v	14.4 (10)
C4—N1—C1—C5	172.9 (6)	N1—C4—C4 ^v —N1 ^v	4.5 (11)
C4—N1—C1—C1 ^v	-2.9 (10)	N3—C6—C7—C8	163.0 (6)
C1—N1—C4—C4 ^v	-1.9 (10)	N3—C6—C7—C11	-19.0 (9)
C6—N3—C5—O1	1.7 (8)	C6—C7—C8—C9	177.0 (6)
C6—N3—C5—C1	-178.5 (4)	C11—C7—C8—C9	-1.1 (9)
C5—N3—C6—C7	-79.7 (7)	C6—C7—C11—C10	-177.5 (6)
Ag1—N4—C9—C8	178.2 (5)	C8—C7—C11—C10	0.5 (9)
C10—N4—C9—C8	0.1 (9)	C7—C8—C9—N4	0.9 (10)
Ag1—N4—C10—C11	-178.8 (5)	N4—C10—C11—C7	0.4 (9)
C9—N4—C10—C11	-0.7 (9)		

Symmetry codes: (i) $x, -y+7/4, -z+3/4$; (ii) $x-1/4, y+1/4, -z+1/2$; (iii) $-x+2, y+1/4, z+1/4$; (iv) $-x+7/4, y, -z+3/4$; (v) $-x+7/4, -y+7/4, z$; (vi) $-x+2, y-1/4, z-1/4$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3N \cdots O11 ^{vii}	0.88	1.86	2.744 (14)	178
N3—H3N \cdots O13 ^{vii}	0.88	2.26	2.875 (13)	127
C4—H4 \cdots O11 ^{viii}	0.95	2.45	3.378 (13)	165
C4—H4 \cdots O14 ^{ix}	0.95	2.40	3.33 (2)	168
C9—H9 \cdots O13 ^x	0.95	2.50	3.224 (14)	133
C11—H11 \cdots O13 ^{vii}	0.95	2.51	3.154 (13)	126

Symmetry codes: (vii) $x, y+1, z$; (viii) $-x+2, -y+1, -z$; (ix) $-x+2, y+3/4, z-1/4$; (x) $x+1/4, y+3/4, -z+1/2$.