

An unprecedented three-dimensional silver(I) cluster built up from pyrazine-2,3-dicarboxylate ligands

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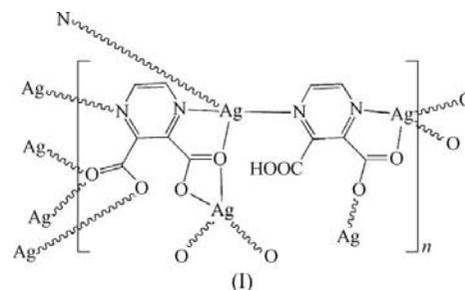
The title complex, poly[(μ -3-carboxypyrazine-2-carboxylato)-(μ -pyrazine-2,3-dicarboxylato)trisilver(I)], $[\text{Ag}_3(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)]_n$ or $[\text{Ag}_3(\text{pzdca})(\text{Hpzdca})]_n$ (H_2pzdca is pyrazine-2,3-dicarboxylic acid), has a three-dimensional structure. The carboxylate groups of the pzdca^{2-} and Hpzdca^- ligands adopt both bridging and chelating coordination modes. Although each Ag^{I} ion displays a tetrahedral coordination, the coordination environment of each Ag atom is very different, *viz.* AgN_3O , AgNO_3 and AgO_4 .

Comment

The design and synthesis of inorganic–organic composite coordination polymers exhibiting novel structures and properties have provided exciting new prospects (Cingolani *et al.*, 2005; Dikarev *et al.*, 2005). To date, a number of monometallic extended inorganic–organic composite materials have been synthesized by the combination of organic spacers and inorganic metal salts (Fujita *et al.*, 1995). At this stage, confidence in accomplishing this goal is based upon the sophisticated selection and utilization of suitable metal ions and 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 (Davis, 2002; Hagrman *et al.*, 1999).

Pyrazine-2,3-dicarboxylic acid (H_2pzdca) and its anions have been of interest in coordination and supramolecular chemistry and they generally tend to react with metal salts to yield insoluble polynuclear materials. The deprotonated pzdca anions (Hpzdca^- and pzdca^{2-}) behave as polyfunctional ligands and are well known to act as bridging ligands in metal complexes (Konar *et al.*, 2004; Beobide *et al.*, 2006; Maji *et al.*, 2004). Various possible coordination modes for the pzdca ligand, such as bidentate, bis(bidentate) bridging and tridentate bridging have been reported (Wenkin *et al.*, 1997; Kondo *et al.*, 1999; Liu *et al.*, 2007). Silver(I) is used as a favourable building block for many coordination architectures, on

account of its metallophilic interaction, short $M-M$ bond and rich variety of coordination geometry, such as linear, bent, trigonal planar, T-shaped, tetrahedral and trigonal pyramidal. Smith and Jaber and their co-workers have reported two-dimensional silver complexes containing H_2pzdca in which the Ag^{I} ions exhibit trigonal–planar geometries (Smith *et al.*, 1995; Jaber *et al.*, 1994). To date, as far as we are aware, there is no three-dimensional Ag^{I} example containing pyrazine-2,3-dicarboxylate. We report here the structure of the title compound, (I).



Compound (I) involves one pzdca^{2-} dianionic ligand, one Hpzdca^- monoanionic ligand and three symmetry-independent Ag^{I} atoms and has a three-dimensional structure. Although each Ag^{I} ion adopts a tetrahedral coordination and the coordination environments are very different (Fig. 1). Atom Ag1 displays an AgN_3O framework, with the pzdca^{2-} dianion acting as a chelating ligand through atoms N4 and O5, the Hpzdca^- monoanion acting as a monodentate ligand through atom N1 and a symmetry-related pzdca^{2-} dianion acting as a monodentate ligand through atom N3. Atom Ag2 exhibits an AgO_3N coordination environment, which consists of the N,O -chelating group from the Hpzdca^- monoanion and two O atoms from different symmetry-related pzdca^{2-} dianions. Atom Ag3 adopts an AgO_4 coordination environment, which consists of two chelating O atoms, O5 and O6, from the same carboxylate group and two monodentate atoms,

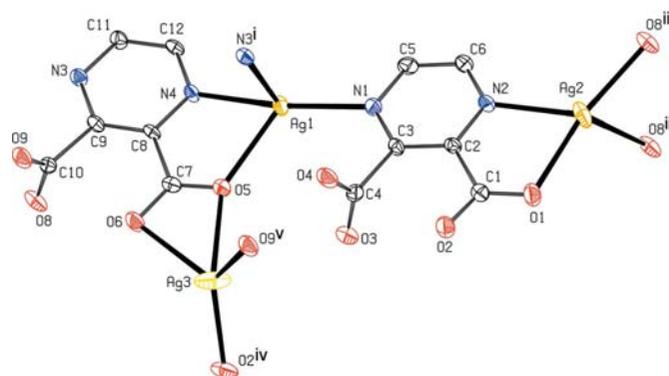


Figure 1
A view of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $1 + x, y - 1, z$; (iii) $2 - x, 1 - y, 1 - z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, 1 - y, 1 - z$.]

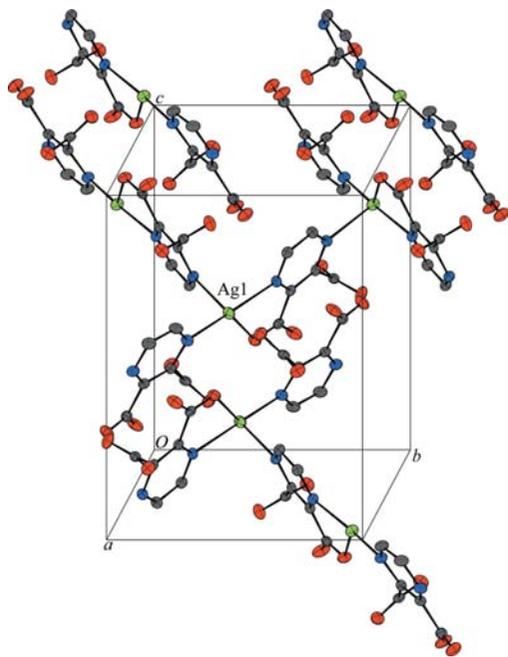


Figure 2
The one-dimensional V-shaped Ag1 chain of (I).

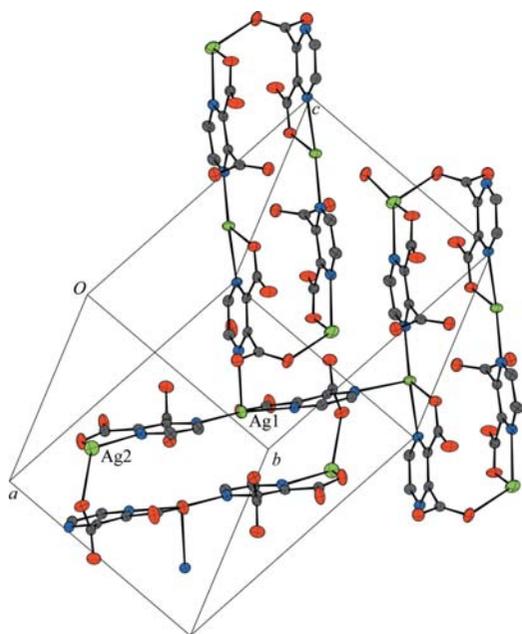


Figure 3
A partial packing view of (I), showing the formation of the two-dimensional sheet built up from Ag1 and Ag2 atoms and pzdc²⁻ dianions.

O2 and O9, from symmetry-related pzdc²⁻ and Hpzdca⁻ ligands. The Ag–O and Ag–N bond lengths (Table 1) are in good agreement with reported values (Dong *et al.*, 2004).

The previously known structures based on the pzdc²⁻ ligand, *viz.* ammonium (pyrazine-2,3-dicarboxylato)silver(I) and ammine(μ -pyrazine-2,3-dicarboxylato)disilver(I) (Smith *et al.*, 1995; Jaber *et al.*, 1994), display two-dimensional poly-

meric sheets. In the two structures, the Ag^I centres exhibit trigonal–planar geometries very different from the coordination reported here for compound (I). Furthermore, the presence of a smaller ammine molecule in the second structure may affect the final packing. In the present work, both N atoms bond to Ag^I ions and the carboxylate groups adopt diverse coordination modes, both chelating and bridging, which are responsible for the building of the three-dimensional structure.

The two dicarboxylates of the pzdc²⁻ ligands of (I) exhibit different bridging modes in the packing. One carboxylate group (C7) of the pzdc²⁻ dianion adopts bidentate–chelating and bridging modes, and the second (C10) shows a tridentate bridging mode. The carboxylate group (C1) of the Hpzdca⁻ monoanion shows a tridentate bridging mode. The carboxyl group (C4) of the Hpzdca⁻ monoanion is not involved in the coordination. Based on these observations, if we only consider atom Ag1, a one-dimensional V-shaped chain is built up from Ag^I ions and both pzdc²⁻ ligands along the *b* axis, as shown in Fig. 2. The Ag1⋯Ag1 separation across the pzdc²⁻ ligand bridge is 7.55 (8) Å. Including atom Ag2 in the V-shaped one-dimensional network leads to a two-dimensional network parallel to the (101) plane, as shown in Fig. 3. Including atom Ag3 links these two-dimensional sheets to build a three-dimensional network. To the best of our knowledge, this is the first example of an Ag–pzdc²⁻ framework constructed from such a unique structural motif.

It may be noted that there is a hydrogen bond between the carboxyl group (O4) and the carboxylate O9 atom at (–*x* + 1, –*y* + 1, –*z* + 1), further stabilizing the Ag–organic framework of (I) (Table 2).

In conclusion, this complicated three-dimensional Ag structure can be described as a new type of Ag coordination polymer, with the pzdc²⁻ ligand acting in monodentate, bidentate and bridging modes.

Experimental

A solution of Na₂(pzdca) (22.5 mg, 0.12 mmol) in methanol (15 ml) was layered on to an aqueous solution of silver acetate (10 mg, 0.025 mmol). The resultant system was kept at room temperature for three weeks and yielded block-shaped crystals of (I).

Crystal data

[Ag ₃ (C ₆ H ₂ N ₂ O ₄)(C ₆ H ₃ N ₂ O ₄)]	<i>V</i> = 1458.7 (7) Å ³
<i>M_r</i> = 656.81	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 11.312 (3) Å	μ = 4.05 mm ⁻¹
<i>b</i> = 10.158 (3) Å	<i>T</i> = 298 (2) K
<i>c</i> = 13.348 (4) Å	0.26 × 0.19 × 0.11 mm
β = 108.004 (5)°	

Data collection

Bruker APEXII area-detector diffractometer	7029 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	2583 independent reflections
<i>T</i> _{min} = 0.419, <i>T</i> _{max} = 0.664	1978 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.031

Table 1

Selected geometric parameters (Å, °).

Ag1—N1	2.237 (4)	Ag2—O1	2.372 (4)
Ag1—N4	2.319 (4)	Ag2—O8 ⁱⁱⁱ	2.470 (4)
Ag1—O5	2.406 (3)	Ag3—O2 ^{iv}	2.249 (3)
Ag1—N3 ⁱ	2.476 (4)	Ag3—O9 ^v	2.368 (4)
Ag2—O8 ⁱⁱ	2.283 (3)	Ag3—O5	2.412 (3)
Ag2—N2	2.326 (4)	Ag3—O6	2.572 (4)
N1—Ag1—N4	165.82 (14)	O8 ⁱⁱ —Ag2—O8 ⁱⁱⁱ	76.63 (13)
N1—Ag1—O5	120.52 (13)	N2—Ag2—O8 ⁱⁱⁱ	120.12 (13)
N4—Ag1—O5	70.68 (12)	O1—Ag2—O8 ⁱⁱⁱ	110.02 (13)
N1—Ag1—N3 ⁱ	98.96 (14)	O2 ^{iv} —Ag3—O9 ^v	124.88 (14)
N4—Ag1—N3 ⁱ	89.07 (14)	O2 ^{iv} —Ag3—O5	132.61 (13)
O5—Ag1—N3 ⁱ	90.73 (13)	O9 ^v —Ag3—O5	92.07 (12)
O8 ⁱⁱ —Ag2—N2	124.09 (14)	O2 ^{iv} —Ag3—O6	115.36 (15)
O8 ⁱⁱ —Ag2—O1	157.94 (13)	O9 ^v —Ag3—O6	118.02 (13)
N2—Ag2—O1	71.85 (13)		

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

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4 \cdots O9 ^v	0.82	1.76	2.568 (5)	169

Symmetry code: (v) $-x + 1, -y + 1, -z + 1$.**Refinement** $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.082$ $S = 1.03$

2583 reflections

245 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.84 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -1.12 \text{ e } \text{Å}^{-3}$

All H atoms attached to C and O atoms were fixed geometrically and treated as riding, with C—H = 0.93 Å (pyridine ring) and O—H = 0.82 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$. Atoms Ag2 and Ag3 display rather large ellipsoids but attempts to model a disordered distribution of these Ag atoms failed. The large ellipsoids might be related to the fact that these two Ag atoms are not tightly bonded to O atoms and have sufficient room to move.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure:

SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3105). Services for accessing these data are described at the back of the journal.

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