

The coordination polymer poly[(μ_3 -3-aminocarbonylpyrazine- 2-carboxylato- $\kappa^3 N^1:O^2:O^2$)silver(I)]

Al-shima'a A. Massoud,^{a*} Vratislav Langer,^a Morsy A. M. Abu-Youssef^b and Lars Öhrström^a

^aDepartment of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Göteborg, Sweden, and ^bDepartment of Chemistry, Faculty of Science, Alexandria University, PO Box 426, Ibrahimia, 21321 Alexandria, Egypt
Correspondence e-mail: shimo@chalmers.se

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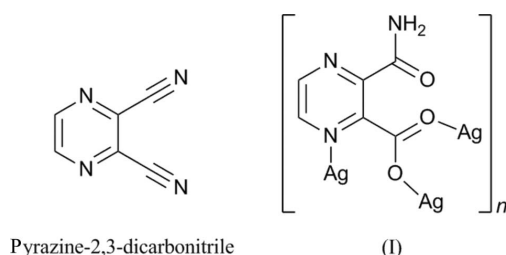
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The title compound, [Ag(C₆H₄N₃O₃)_n or [Ag(pyzca)]_n (where pyzca is 3-aminocarbonylpyrazine-2-carboxylate), (I), was obtained by silver-catalysed partial hydrolysis of pyrazine-2,3-dicarbonitrile in aqueous solution. The compound has a distorted trigonal–planar coordination geometry around the Ag^I ion, with each ligand bridging three Ag^I ions to form a one-dimensional strand of molecules parallel to the *b* axis. An extensive hydrogen-bond pattern connects these strands to form a three-dimensional network of **mog** topology.

Comment

The design of metal coordination polymers has attracted considerable interest, particularly with respect to supramolecular chemistry. The choice of ligands coordinated to the metal centres is often the most important factor (Batten *et al.*, 2009). We attempted to synthesize a new silver(I) compound with high dimensionality using the *N:N'*-bridging ligand pyrazine-2,3-dicarbonitrile, but unexpectedly obtained the title silver(I) compound, (I), with the ligand 3-aminocarbonylpyrazine-2-carboxylate (pyzca).



Pyzca is an intermediate compound formed during hydrolysis of the corresponding dicarboxamide to the dicarboxylic acid. Only two structures containing this ligand were found in the Cambridge Structural Database (CSD, updated August 2010; Allen, 2002): [Ni(pyzca)₂(H₂O)₂]·H₂O was obtained upon hydrolysis of pyrazine-2,3-dicarboxamide catalysed by

Ni(NO₃)₂ (Heyn & Dietzel, 2007), while [Co(tren)(pyzca)]-(ClO₄)Cl [where tren is tris(2-aminoethyl)amine] (Mukhopadhyay *et al.*, 2009) was obtained *via* direct reaction of the pyzca ligand with [Co(tren)Cl₂]Cl and NaClO₄ in water. In both these monomeric compounds, pyzca acts as an *N,O*-chelating ligand. Compound (I) is the first coordination polymer obtained from partial hydrolysis of pyrazine-2,3-dicarbonitrile in an aqueous medium. The reaction was relatively slow, catalysed by AgNO₃ (Heyn & Dietzel, 2007) as a Lewis acid, and hence only a few crystals were formed.

A search of the CSD revealed no structures containing the commercially available pyrazine-2,3-dicarbonitrile (the starting ligand), *i.e.* not even the structure of the ligand has yet been determined. For pyrazine-2,3-dicarboxamide, four Cu^{II} structures (Mondal & Ray, 1977; Klein *et al.*, 1983) with the ligand in an *N,O*-chelating mode and one Ag^I structure (Massoud *et al.*, 2009) with the ligand in an *N:N'*-bridging mode have been reported. In contrast, many compounds of pyrazine-2,3-dicarboxylic acid with alkali (Tombul *et al.*, 2006, 2007; Tombul, Güven & Büyükgüngör, 2008; Tombul, Güven & Svoboda, 2008; Tombul & Guven, 2009) and transition metals (Zou *et al.*, 1998, 1999; Konar *et al.*, 2004; Xu *et al.*, 2008) have been synthesized and structurally characterized.

The structure and atom-numbering scheme for (I) are shown in Fig. 1. The Ag^I ion is coordinated by three ligands, two *via* one carboxylate O atom and one *via* a ring N atom, forming a distorted trigonal–planar geometry at the Ag^I ion. The pyzca ligand acts as an *N:O:O'*-bridging ligand to three Ag^I ions, while the amide group (O81 and N82) and the second pyrazine ring N atom (N4) serve as hydrogen-bond donors or acceptors. The Ag^I ions deviate from the plane of the pyrazine ring, with torsion angles O71ⁱ–Ag1–N1–C2 = 41.7 (4)°, O72ⁱⁱ–Ag1–N1–C2 = –150.3 (4)°, O71ⁱ–Ag1–N1–C6 = –151.2 (3)° and O72ⁱⁱ–Ag1–N1–C6 = 16.8 (3)° (symmetry codes as in Fig. 1). This coordination geometry leads to the formation of successive eight- and ten-membered rings building up an infinite one-dimensional strand of molecules parallel to the *b* axis, with the free amide groups

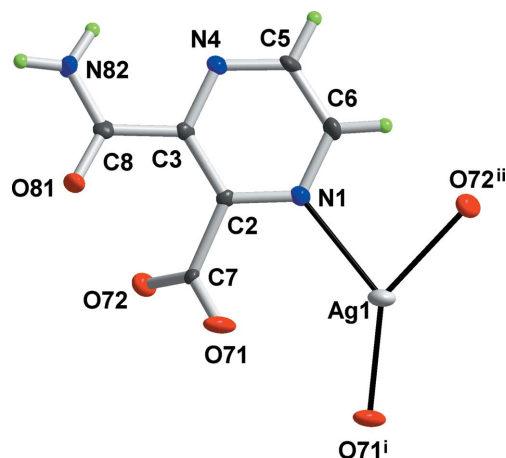
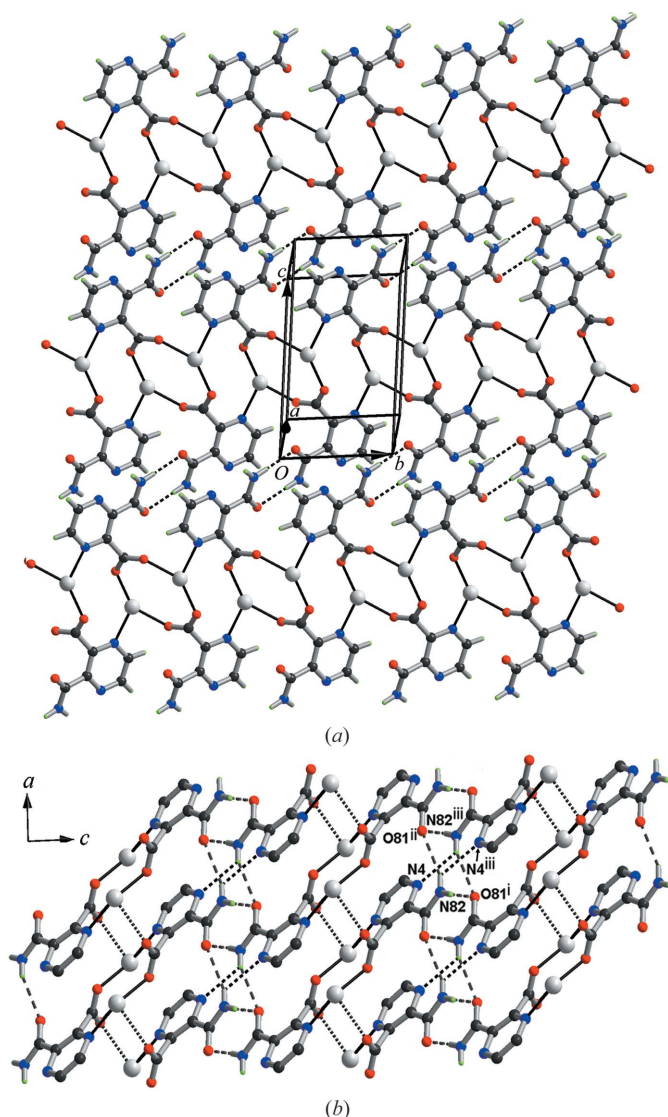


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x, y - 1, z$.]


Figure 2

(a) A perspective view of (I), perpendicular to $(10\bar{1})$, showing the eight- and ten-membered rings building up a one-dimensional strand parallel to the b axis. $N-H\cdots O$ hydrogen bonds (dashed lines) connect the one-dimensional strands to form a two-dimensional sheet. (b) A perspective view of (I), showing the eight- and ten-membered rings formed *via* both $N-H\cdots O$ (long-dashed lines) and $N-H\cdots N$ (short-dashed lines) hydrogen bonds, which extend the structure into a three-dimensional network. The shortest $Ag\cdots O$ interactions are drawn as dotted lines, where the $Ag\cdots O$ distance is 2.714 (3) Å. Atoms H5 and H6 have been omitted for clarity. [Symmetry codes: (iii) $-x+1, -y+2, -z+2$; (iv) $x+1, y, z$; (v) $-x+2, -y+1, -z+2$.]

projecting outwards. Similar strands were found in $\{[NH_4][Ag(\text{pyrazine-2,3-dicarboxylato})]\}_n$ (Smith *et al.*, 1995) and $\{[Ag_2(\text{pyrazine-2,3-dicarboxylato})(NH_3)]\}_n$ (Jaber *et al.*, 1994), where ten- and 14-membered rings were formed instead. Selected bond distances and angles for (I) and for related Ni^{II} (Heyn & Dietzel, 2007), Co^{II} (Mukhopadhyay *et al.*, 2009) and Ag^I (Smith *et al.*, 1995; Jaber *et al.*, 1994) compounds are compared in Table 1. In contrast with the four above-mentioned compounds, (I) has a longer metal–nitrogen bond distance. The Ni^{II} (Heyn & Dietzel, 2007) and Co^{II}

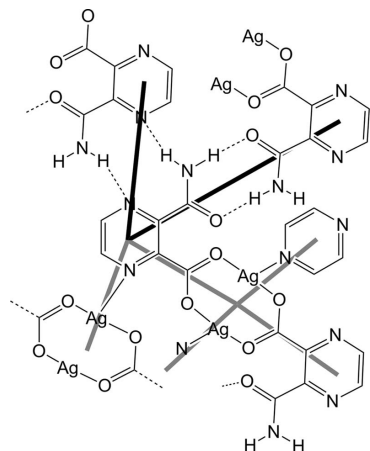
(Mukhopadhyay *et al.*, 2009) compounds have much shorter bond distances, associated with their smaller metal ionic radii, while the two Ag^I –pyrazine-2,3-dicarboxylate compounds (Smith *et al.*, 1995; Jaber *et al.*, 1994) have distances and angles comparable with those of (I), consistent with their similar topology.

Extensive inter- and intramolecular hydrogen bonds of $N-H\cdots O$, $N-H\cdots N$ and $C-H\cdots O$ types (Table 2) connect the one-dimensional strands of (I). The hydrogen bonds between opposite amide groups ($N82-H82A\cdots O81^{iii}$; symmetry codes as in Fig. 2) form inversion-symmetric eight-membered rings, with a graph-set symbol (Bernstein *et al.*, 1995) of $R_2^2(8)$, extending the structure to form a two-dimensional sheet (Fig. 2a). The plane of the strands is $(10\bar{2})$, whereas the sheets lie parallel to $(10\bar{1})$. Almost perpendicular to this strong and well known supramolecular synthon we find a three-centre amide–pyrazine hydrogen-bond system forming eight- ($N82-H82B\cdots O81^{iv}$) and ten-membered rings ($N82-H82B\cdots N4^{iv}$) with graph-set symbols of $R_2^2(8)$ and $R_2^2(10)$, respectively, which further extends the structure to form a three-dimensional network (Fig. 2b).

Often a clearer description and better understanding of such a structure can be obtained by network analysis, a concept introduced by Wells (1954, 1977) and further developed by O’Keeffe and others (O’Keeffe & Hyde, 1996). Recently, we have successfully used this technique on a number of hydrogen-bonded systems (Abu-Youssef *et al.*, 2006; Johansson *et al.*, 2007; Wallentin *et al.*, 2009). Briefly, the method involves finding the topology symbol [a three letter code, often preceded by the point symbol (or Schläfli symbol)] of the net, describing the number of different rings (O’Keeffe *et al.*, 2010; Blatov *et al.*, 2010) of the three-dimensional net, and this then gives a reduced, and often informative, description of the structure. The structures can thus, in many cases, be related to a small number of high-symmetry nets (Ockwig *et al.*, 2005) found from geometric considerations or from inorganic-type structures and minerals.

The first step in such an analysis is to assign nodes, and in this case the Ag eight-membered ring in the one-dimensional strand is an obvious choice as it clearly connects to four different ligands. For further analysis of the hydrogen-bond connectivities, simplicity is one of the main guidelines; a net with high symmetry that contributes to the understanding of the structure is better than a complicated multinodal net that might not even have been recorded previously. Thus, we consider the strong double $N82-H82A\cdots O81^{iii}$ hydrogen bonds and the likewise strong double $N82-H82B\cdots N4^{iv}$ hydrogen bonds as forming the links between the ligands and two Ag dimeric nodes, and two other ligands giving a network with two different four-connected vertices. In doing so, we ignore not only the intramolecular $N82-H82B\cdots N4$ hydrogen bonds but also the $N82-H82B\cdots O81^{iv}$ interaction. The latter is clearly much weaker than the $N82-H82A\cdots O81^{iii}$ hydrogen bond of the same type, and, considering the larger covalent radius of N compared with O (Bondi, 1964), also weaker than the $N82-H82B\cdots N4^{iv}$ interaction. However, more importantly, this interaction does not connect

two ligands to each other; instead, it forms a double hydrogen-bond motif connecting four ligands. Thus, a network description incorporating this intermolecular bond as well would give a complicated three-nodal net and we would not gain anything in terms of describing or understanding the structure.



The complete assignment, shown in the scheme above, gives three- and four-connected nets. The Ag^{I} node is close to

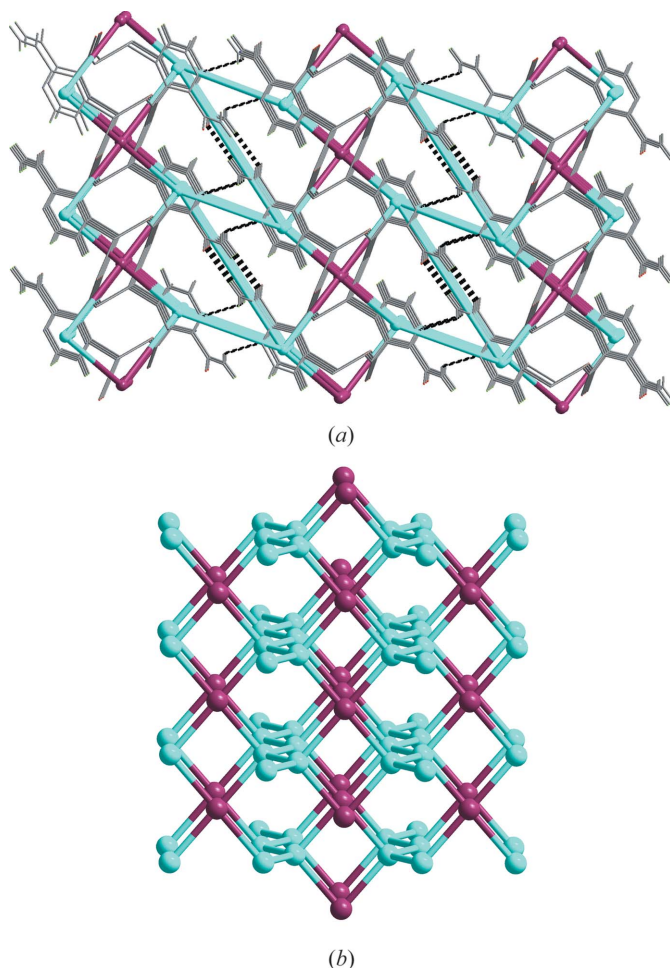


Figure 3
(a) A perspective view of (I), showing the three-dimensional (**mog** net) structure supported by N–H···O and N–H···N hydrogen bonds (dashed lines). (b) A perspective view, showing the ideal **mog** net.

square planar (angles = 109 and 71°), but the pyzca node has a very distorted geometry, as shown in Fig. 3(a), compared with the ideal **mog** net topology shown in Fig. 3(b) (see discussion below).

Analysis of the resulting topology using the *SYSTRE* program (Delgado Friedrichs, 2007) shows that the net belongs to a class of binodal networks combining square-planar and tetrahedral nodes, and more specifically a $(4^2.6^2.8^2)_2(4.6^4.8)$ -**mog** net (from the mineral moganite) (Delgado Friedrichs *et al.*, 2003; Öhrström & Larsson, 2005; O’Keeffe *et al.*, 2008). The most common topology of this type of topology is the **pts** net (Ockwig *et al.*, 2005), and only a few examples are known of the **mog** net (Kostakis *et al.*, 2009).

Some weaker Ag···O and Ag···Ag interactions with other strands above and below the parent strand support the three-dimensional structure [$\text{Ag1}\cdots\text{O72}^{\text{viii}} = 2.714(3) \text{ \AA}$, $\text{Ag1}\cdots\text{O71} = 2.956(4) \text{ \AA}$, $\text{Ag1}\cdots\text{O72}^{\text{i}} = 3.3010(4) \text{ \AA}$ and $\text{Ag1}\cdots\text{Ag1}^{\text{vii}} = 3.4000(6) \text{ \AA}$; symmetry codes: (i) $-x, 1-y, 1-z$; (vii) $-x, -y, 1-z$; (viii) $1-x, 1-y, 1-z$], as well as the aforementioned weaker amide–amide interaction.

The Ag···Ag interaction is at the limit of the double van der Waals radius of silver (Bondi, 1964), and was therefore neglected when assigning the network structure. No π – π stacking could be found between pyrazine rings.

Experimental

An ethanolic solution of pyrazine-2,3-dicarbonitrile (0.5 g, 4 mmol) was added to an aqueous solution of AgNO_3 (0.34 g, 2 mmol). The mixture was allowed to stand undisturbed for one month in the dark. Colourless plates of (I) suitable for X-ray measurements were collected and dried in air, with a yield of ~10% relative to Ag.

Crystal data

$[\text{Ag}(\text{C}_6\text{H}_4\text{N}_3\text{O}_3)]$	$\gamma = 84.509(2)^\circ$
$M_r = 273.99$	$V = 344.13(2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 5.0540(2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 6.2507(2) \text{ \AA}$	$\mu = 2.90 \text{ mm}^{-1}$
$c = 10.9778(2) \text{ \AA}$	$T = 153 \text{ K}$
$\alpha = 85.570(1)^\circ$	$0.04 \times 0.04 \times 0.02 \text{ mm}$
$\beta = 88.638(1)^\circ$	

Data collection

Siemens SMART CCD area-detector diffractometer	5479 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2079 independent reflections
$T_{\text{min}} = 0.228, T_{\text{max}} = 0.944$	1540 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.091$	$\Delta\rho_{\text{max}} = 1.01 \text{ e \AA}^{-3}$
$S = 1.01$	$\Delta\rho_{\text{min}} = -1.02 \text{ e \AA}^{-3}$
2079 reflections	
126 parameters	
1 restraint	

Aromatic H atoms were constrained to ideal geometry, with $\text{C}–\text{H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The amino H atoms were located in a difference Fourier synthesis map and refined isotropi-

Table 1

Selected bond distances and angles (Å, °) for (I) and some related compounds.

Note that only bonds involving pyzca and pyrazine-2,3-dicarboxylic acid ligands are mentioned.

Compound	Distance	Angle
(I)	Ag1–N1	2.385 (4)
	Ag1–O71 ⁱ	2.218 (3)
	Ag1–O72 ⁱⁱ	2.324 (3)
	Ni–N	2.0724 (13)
[Ni(pyzca) ₂ ·(H ₂ O) ₂]·H ₂ O ^d	Ni–O	2.0403 (11)
	N–Ni–N	174.21 (5)
[Co(tren)(pyzca)]·(ClO ₄)Cl ^b	Co–N	1.88 (2)
	Co–O	1.941 (13)
[[Ag(C ₆ H ₂ N ₂ O ₄)] _n ·[NH ₄]] ^c	Ag–N	2.249 (6)
	Ag–O	2.333 (6)
[[Ag ₂ (C ₆ H ₂ N ₂ O ₄)(NH ₃)] _n ^d	Ag–N	2.277 (3)
	Ag–O	2.312 (4)
	O–Ag–O	136.8 (1)
	O–Ag–O	93.2 (1)

References: (a) Heyn & Dietzel (2007); (b) Mukhopadhyay *et al.* (2009); (c) Smith *et al.* (1995); (d) Jaber *et al.* (1994). Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x, y - 1, z$.

cally, with the N–H distances restrained to be similar, having an s.u. of 0.02 Å. The maximum feature of the residual electron density is 1.20 e Å⁻³, close to the Ag^I atom.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT and SADABS (Sheldrick, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2010); software used to prepare material for publication: SHELXTL (Sheldrick, 2008) and SYSTRE (Delgado Friedrichs, 2007); topology codes from the RCSR (O’Keeffe *et al.*, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3193). Services for accessing these data are described at the back of the journal.

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Table 2

Hydrogen-bond geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
N82–H82A···O81 ⁱⁱⁱ	0.85 (5)	2.12 (5)	2.947 (5)	165 (6)
N82–H82B···O81 ^{iv}	0.87 (5)	2.59 (6)	3.123 (6)	121 (6)
N82–H82B···N4	0.87 (5)	2.27 (7)	2.678 (6)	109 (5)
N82–H82B···N4 ^v	0.87 (5)	2.63 (6)	3.198 (6)	125 (6)
C5–H5···O81 ^{vi}	0.95	2.37	3.307 (5)	170
C6–H6···O72 ⁱⁱ	0.95	2.42	3.032 (6)	122

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

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