

Bis(1,3,5-triazine-2,4,6-triamine- κ N¹)-silver(I) nitrate

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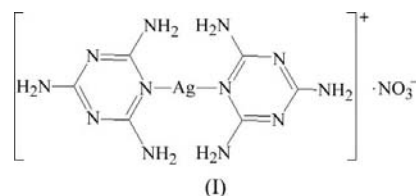
The title compound, [Ag(C₃H₆N₆)₂]⁺NO₃⁻, has an alternating two-dimensional bilayer structure supported by extensive hydrogen bonds. The [Ag(melamine)₂]⁺ cationic monomers (melamine is 1,3,5-triazine-2,4,6-triamine) are connected *via* N—H···N hydrogen bonds to form two-dimensional sheets. Nitrate groups are sandwiched between two sheets through N—H···O hydrogen bonds. An almost perfectly linear coordination geometry is found for the Ag^I ions. The triazine ligands are slightly distorted due to π – π interactions.

Comment

Silver(I) is able to form linear (Greenwood & Earnshaw, 1997), trigonal–planar or tetrahedral coordination geometries due to the presence of vacant *s* and *p* orbitals. Our ongoing research concerns the synthesis, structure and biological activity of different silver(I) compounds with pyridine-type ligands (Abu-Youssef *et al.*, 2007) and especially aminopyridines (Abu-Youssef *et al.*, 2006*a,b*). Melamine is considered an interesting ligand from a supramolecular chemistry point of view, due to the presence of three donor and three acceptor N atoms. This makes the probability of achieving three-dimensional network structures *via* melamine–metal coordination bonds and melamine–melamine hydrogen bonds much greater than with pyridines and pyrazines. Melamine is also used as a co-ligand to extend the dimensionality of a structure when poor coordinating ligands are used (Zhang *et al.*, 2004). Although melamine–melamine hydrogen bonds facilitate the solubility of the ligand in water, coordination of the ligand to metals is not easy, and once the compound is formed the solubility decreases. Against this background, we have prepared the title silver(I)–melamine complex, (I), and present its structure here.

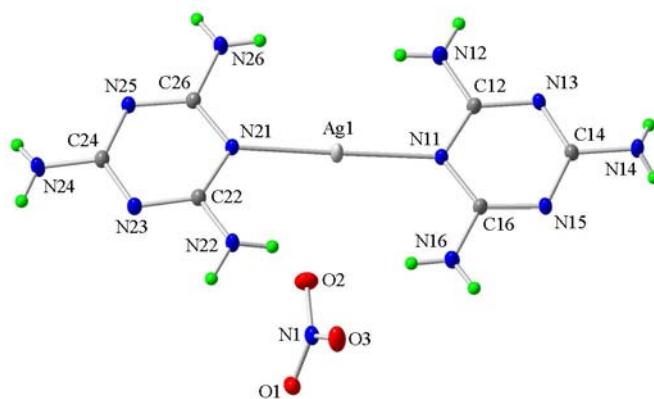
The silver(I) centre of (I) is coordinated to two monodentate melamine ligands, each through one of its triazine ring N atoms, forming a linear coordination geometry around the silver(I) ion (Fig. 1). The Ag–N bond distances are slightly

longer than those reported for [Ag(melamine)₂]⁺ClO₄⁻ (Zhu *et al.*, 1999) and shorter than those reported for [Ag(NO₃)(melamine)]_n (Sivashankar *et al.*, 2001), while the N–Ag–N bond angle is larger than those found in the above-mentioned compounds (Table 2). Only a weak interaction between the Ag^I ion and the nitrate group is found, with geometric values almost identical to those observed for [Ag(melamine)₂]⁺ClO₄⁻ (Zhu *et al.*, 1999) (Table 2). A similar interaction was also found in [Ag(NO₃)(melamine)]_n, where Ag–O1 is 2.569 (2) Å (Table 2) with a distorted trigonal–planar coordination geometry around the Ag^I ion.

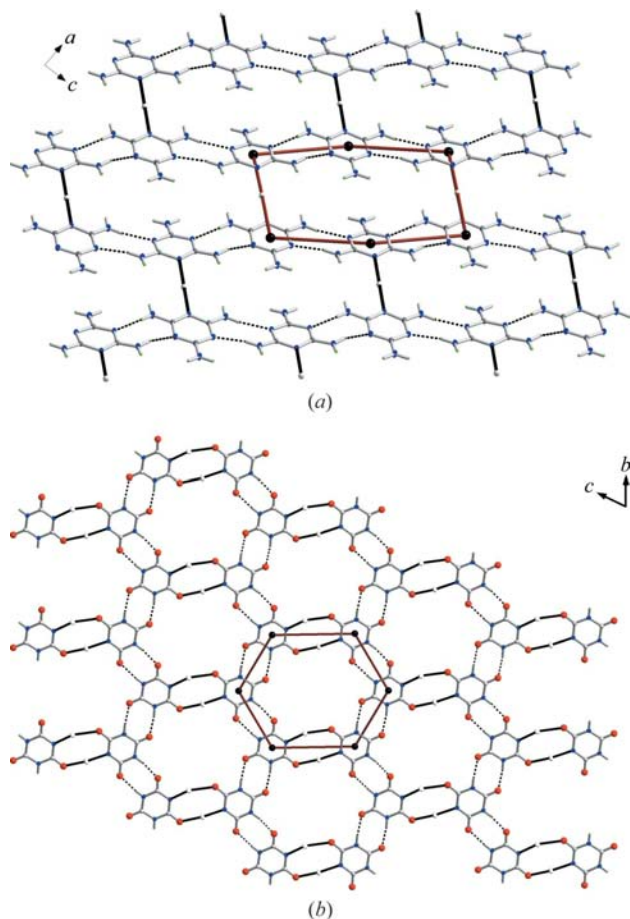


Strong N—H···N hydrogen bonds (Table 1) connect the cationic [Ag(melamine)₂]⁺ units of (I) to form a two-dimensional honeycomb sheet (Fig. 2*a*). This two-dimensional honeycomb sheet is best described as a chain of N—H···N hydrogen-bonded melamine ligands connected by Ag^I ions. The N—H···N hydrogen bonds in (I) [*D*···*A* = 3.013 (2)–3.041 (2) Å and *D*–H···*A* = 170 (2)–177 (3)°] are much stronger than those found in [Ag(NO₃)(melamine)]_n (*D*···*A* = 3.077 Å and *D*–H···*A* = 159°).

A similar double-layer honeycomb structure was found for a compound of Ag^I with isocyanurate, [Ag₄(C₃N₃H₂O₃)₄-(bpy)] (bpy is 4,4'-bipyridine; Zhang *et al.*, 2007) (Fig. 2*b*), in which the bilayer sheets are connected *via* bpy ligands to form a three-dimensional network structure. The two-dimensional honeycomb sheets in this isocyanurate compound are formed through shorter N—H···O hydrogen bonds [2.836 (4)–2.891 (4) Å]. Both this compound and (I) exhibit the same type of hydrogen-bonded ring, a small one with graph-set symbol *R*₂²(8) (Bernstein *et al.*, 1995), formed through direct hydrogen bonding between melamine ligands in (I) and between isocyanurate ligands in [Ag₄(C₃N₃H₂O₃)₄-(bpy)].


Figure 1

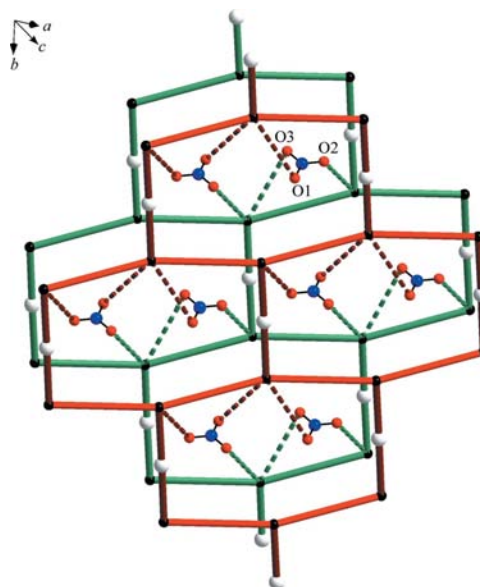
A perspective drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 2**

(a) Projection of the structure of (I) along the *b* axis, showing the two-dimensional honeycomb sheet formed *via* N–H···N hydrogen bonds (dashed lines) between melamine ligands. The large six-membered ring shows four $R_2^2(8)$ motifs. Nitrate anions have been omitted for clarity. (b) Projection of the structure of $[Ag_4(C_3N_3H_2O_3)_4(bpy)]$ (Zhang *et al.*, 2007) along the *a* axis, showing a similar two-dimensional honeycomb sheet formed *via* N–H···O hydrogen bonds (dashed lines). The large six-membered ring encompasses four $R_2^2(8)$ motifs. Bipyridine molecules have been omitted for clarity.

Although compound (I) and $[Ag(melamine)_2]ClO_4$ have a common cation, they pack differently, and only a ladder structure is formed *via* N–H···N hydrogen bonds for the latter. This can be attributed to the difference in size between the nitrate and perchlorate counter-ions. The smaller nitrate anions in (I) are firmly sandwiched between the above-mentioned hydrogen-bonded sheets *via* N–H···O hydrogen bonds, resulting in the formation of another bilayer hydrogen-bonded two-dimensional sheet of molecules. The thickness of this bilayer sheet is larger than the sum of the van der Waals radii for two silver(I) ions (3.40 Å; Zhang *et al.*, 2007), with an Ag···Ag distance of 3.924 (3) Å, in contrast with $[Ag_4(C_3N_3H_2O_3)_4(bpy)]$, where the Ag···Ag distance is 3.004 Å, which confirms a higher interaction within the sheet.

There are 11 different N–H···O interactions observed in (I) (Table 1). Only those with $D\cdots A$ distances in the range 2.969 (2)–3.271 (2) Å and $D-H\cdots A$ angles in the range 146 (2)–170 (3)° are considered strong hydrogen bonds, but

**Figure 3**

A perspective view of (I), showing how the nitrate anions support the structure, being alternately sandwiched between two sheets of $[Ag(melamine)_2]^+$ through extensive N–H···O hydrogen bonds (dashed lines). (In the electronic version of the paper, the upper sheet is red and the lower sheet is green, and melamine ligands are shown as black spheres.)

they are still weaker than those found in $[Ag(NO_3)(melamine)]_n$ ($D\cdots A = 3.177$ and 3.198 Å, and $D-H\cdots A = 169$ and 178°). Fig. 3 shows two cationic sheets of $[Ag(melamine)_2]^+$ and illustrates how the nitrates are packed between them, mainly through atoms O1, connected to the upper sheet, and O3, connected to the lower sheet, *via* hydrogen bonds to the NH_2 groups of the melamine ligands. The N–H···O hydrogen bonds in (I) are weaker than the N–H···N hydrogen bonds. Melamine acts as a bridging ligand in the case of $[Ag(NO_3)(melamine)]_n$, giving rise to a one-dimensional zigzag structure which is extended into a three-dimensional structure *via* both N–H···N and N–H···O hydrogen bonds.

The angle between the mean planes of the triazine rings of (I) is $8.5(1)^\circ$. The triazine rings show some distortion due to hydrogen bonding and π – π interactions. Normally, π – π stacking takes place only when the rings are parallel displaced (offset or slipped stacking), and the angle between the centroid-to-centroid vector and the normal of the ring should be around 20° and the centroid-to-centroid distances up to 3.8 Å (Janiak, 2000). In compound (I), the centroid-to-centroid distance is 3.821 (2) Å, the perpendicular distance from the centroid to the plane of the opposite ring is 3.6 Å and the angle between the centroid-to-centroid vector and the normal of the ring is 17.8° , close to normal π – π stacking values. Such π -system aggregates are stabilized by the polar solvent effect (Janiak, 2000). This can account for the insolubility observed for compound (I) in water.

Experimental

To an aqueous solution (4 ml) of $AgNO_3$ (0.34 g, 2 mmol) was added a methanolic solution (2 ml) of the melamine ligand (0.5 g, 4 mmol).

When a white gelatinous precipitate had formed, drops of 0.1 N HNO₃ were added. The mixture was then heated and stirred to dissolve most of the precipitate. The turbid solution was filtered and allowed to stand for a couple of days. Colourless needles of (I) suitable for X-ray diffraction measurements were collected and dried in air (yield ~60% relative to the metal). ¹H NMR in dimethyl sulfoxide gave only one peak at δ(6H) = 6.34 p.p.m.

Crystal data

[Ag(C ₃ H ₆ N ₆) ₂]NO ₃	γ = 67.998 (1)°
M _r = 422.16	V = 659.00 (7) Å ³
Triclinic, P $\bar{1}$	Z = 2
a = 7.9908 (5) Å	Mo Kα radiation
b = 9.8312 (6) Å	μ = 1.58 mm ⁻¹
c = 10.0569 (6) Å	T = 153 K
α = 64.296 (1)°	0.14 × 0.06 × 0.05 mm
β = 77.915 (1)°	

Data collection

Bruker SMART CCD area-detector diffractometer	11902 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	4651 independent reflections
T _{min} = 0.810, T _{max} = 0.925	3957 reflections with I > 2σ(I)
	R _{int} = 0.027

Refinement

R[F ² > 2σ(F ²)] = 0.029	256 parameters
wR(F ²) = 0.071	All H-atom parameters refined
S = 1.00	Δρ _{max} = 0.99 e Å ⁻³
4651 reflections	Δρ _{min} = -0.94 e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N12—H12A...N23 ⁱ	0.83 (3)	2.21 (3)	3.032 (2)	177 (3)
N12—H12B...O1 ⁱⁱ	0.82 (3)	2.23 (3)	2.901 (2)	139 (3)
N12—H12B...O2 ⁱⁱ	0.82 (3)	2.52 (3)	3.201 (2)	141 (3)
N14—H14A...O1 ⁱⁱⁱ	0.70 (3)	2.27 (3)	2.969 (2)	170 (3)
N14—H14B...O3 ⁱ	0.77 (3)	2.26 (3)	3.012 (2)	165 (3)
N16—H16A...N25 ^{iv}	0.81 (3)	2.20 (3)	3.013 (2)	176 (3)
N16—H16B...O3	0.84 (3)	2.22 (3)	2.909 (2)	139 (2)
N16—H16B...O2	0.84 (3)	2.54 (3)	3.271 (2)	146 (2)
N22—H22A...N13 ^v	0.87 (3)	2.18 (3)	3.041 (2)	170 (2)
N22—H22B...O3	0.84 (3)	2.38 (3)	3.013 (2)	132 (2)
N22—H22B...O2	0.84 (3)	2.46 (3)	2.982 (2)	121 (2)
N24—H24A...O3 ^{vi}	0.75 (3)	2.31 (3)	3.044 (2)	163 (3)
N24—H24B...O1 ^{vii}	0.81 (3)	2.25 (3)	3.016 (2)	160 (2)
N26—H26A...O1 ⁱⁱ	0.81 (3)	2.48 (3)	2.972 (2)	120 (2)
N26—H26B...N15 ^{vi}	0.83 (3)	2.21 (3)	3.034 (2)	174 (3)

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

H atoms were located in a difference Fourier map and refined freely in an isotropic approximation.

Table 2

Comparison of Ag—N bond lengths (Å), N—Ag—N angles (°) and Ag...O interactions (Å) in some related compounds.

Compound	Ag—N	Ag—N	N—Ag—N	Ag...O
[Ag(melamine) ₂]NO ₃ , (I)	2.1925 (16)	2.2083 (16)	178.58 (6)	2.7924 (16)
[Ag(melamine) ₂]ClO ₄ ^t	2.162 (4)	2.179 (4)	167.7 (2)	2.776 (4), 2.785 (6)
[Ag(NO ₃)(melamine)] _n ^b	2.289 (2)	2.260 (2)	127.2 (6)	2.569 (2)

References: (a) Zhu *et al.* (1999); (b) Sivashankar *et al.* (2001).

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, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3109). Services for accessing these data are described at the back of the journal.

References

- Abu-Youssef, M., Dey, R., Gohar, Y., Massoud, A., Öhrström, L. & Langer, V. (2007). *Inorg. Chem.* **46**, 5893–5903.
- Abu-Youssef, M., Langer, V. & Öhrström, L. (2006a). *Chem. Commun.* pp. 1082–1084.
- Abu-Youssef, M., Langer, V. & Öhrström, L. (2006b). *Dalton Trans.* pp. 2542–2550.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brandenburg, K. (2008). *DIAMOND*. Version 3.1f. Crystal Impact GbR, Bonn, Germany.
- Bruker (2003). *SMART* (Version 5.63) and *SAINTE* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
- Greenwood, N. N. & Earnshaw, A. (1997). In *Chemistry of the Elements*, 2nd ed. Oxford: Pergamon Press.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sivashankar, K., Ranganathan, A., Pedireddi, V. & Rao, C. (2001). *J. Mol. Struct.* **559**, 41–48.
- Zhang, J., Li, Z.-J., Wen, Y.-H., Kang, Y., Cheng, J.-K. & Yao, Y.-G. (2004). *J. Mol. Struct.* **697**, 185–189.
- Zhang, J., Shen, Y.-C., Qin, Y.-Y., Li, Z.-J. & Yao, Y.-G. (2007). *CrystEngComm*, **9**, 636–639.
- Zhu, H., Yu, Z., You, X., Hu, H. & Huang, X. (1999). *J. Chem. Crystallogr.* **29**, 239–242.