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Diamminesilver(I) bis(2-amino-5-nitrobenzoato-$\kappa^2O^1,O^{1'}$)silver(I): a two-dimensional supramolecular sheet with a short intersheet distance containing a rare four-coordinate planar silver(I) centre

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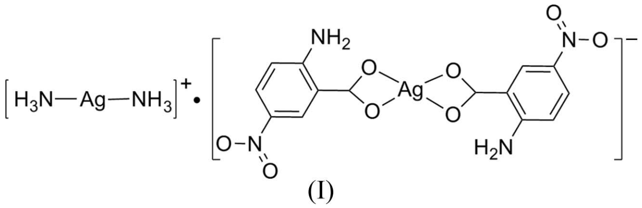
The asymmetric unit of the title compound, $[Ag(NH_3)_2][Ag(C_7H_5N_2O_4)_2]$, comprises half an $[Ag(NH_3)_2]^+$ cation and half an $[Ag(anbz)_2]^-$ anion (anbz is 2-amino-5-nitrobenzoate). Both Ag^I ions are located on inversion centres. The cation has a linear coordination geometry with two symmetry-related ammine ligands. The Ag^I cation in the anionic part shows a rare four-coordinate planar geometry completed by two chelating symmetry-related anbz ligands. Intra- and intermolecular N—H⋯O hydrogen bonds create a slightly undulating two-dimensional supramolecular sheet. Adjacent sheets are only *ca* 3.3 Å apart. Ag⋯O, Ag⋯N and π–π stacking interactions consolidate the packing of the molecules in the solid state.

Comment

In coordination chemistry, silver in the +1 oxidation state is found to adopt a wide variety of coordination geometries due to the lack of stereochemical preference arising from a d^{10} closed-shell configuration (Blake, Brooks *et al.*, 1999; Blake, Champness *et al.*, 1999; Blake *et al.*, 1997; Batten & Robson 1998; Yaghi *et al.*, 2003). Coordination numbers for Ag^I from 2 to 8 have been observed (without including Ag⋯Ag interactions), often with distorted coordination geometries owing to the inherent lack of CFSE (crystal field stabilization energy). However, square-planar Ag^I stereochemistry is generally acknowledged as rare (Young & Hanton, 2008); the first structurally characterized square-planar Ag^I complex was a flavin complex (Fritchie, 1972). On the other hand, although Ag^I under ammoniacal conditions can form $[Ag(NH_3)_2]^+_n$ cations ($n = 1$ or 2) (Zheng *et al.*, 2007), which can be stabilized by supramolecular interactions, only a limited number of $[Ag(NH_3)_2]$-containing complexes have been documented, due to the weak $Ag—N_{ammine}$ coordination bond (Zheng *et al.*, 2002; You *et al.*, 2004; Pajunen & Pajunen 1994; Paul *et al.*, 2005; Zheng *et al.*, 2008; Whitcomb & Rajeswaran 2008). 2-Amino-5-nitrobenzoate (H_2anbz) is a multifunctional ligand which can form not only the usual Ag—O coordination bonds through its carboxyl group, but also Ag⋯O and Ag⋯N weak interactions and hydrogen bonds using its amino and nitro groups. However, the silver(I)–anbz complex has not been reported until now. Recently, we reported some other silver(I) complexes (Sun, Luo, Huang *et al.*, 2009; Sun, Luo, Xu *et al.*, 2009; Sun, Luo *et al.*, 2010; Sun, Zhang, Luo *et al.*, 2010; Sun, Zhang, Xu *et al.*, 2010), and as an extension of our work on the structural characterization of silver(I) complexes, the title complex, (I), is reported here.



(I)

The asymmetric unit in the structure of complex (I) comprises half an $[Ag(NH_3)_2]^+$ cation and half an $[Ag(anbz)_2]^-$ anion (Fig. 1). Each Ag^I ion is on a special position associated with the crystallographic inversion centre. One Ag^I

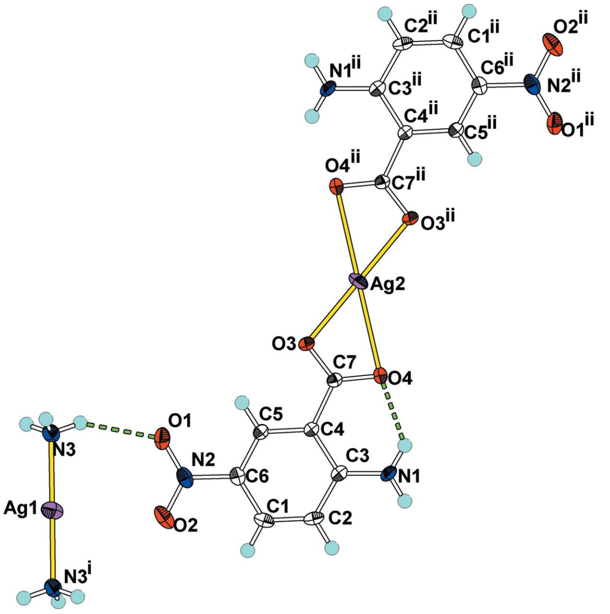


Figure 1
The structure of (I), showing the atom-numbering scheme and the coordination environment around the two different Ag^I centres. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 2, -y + 2, -z$; (ii) $-x + 2, -y + 1, -z + 2$.]

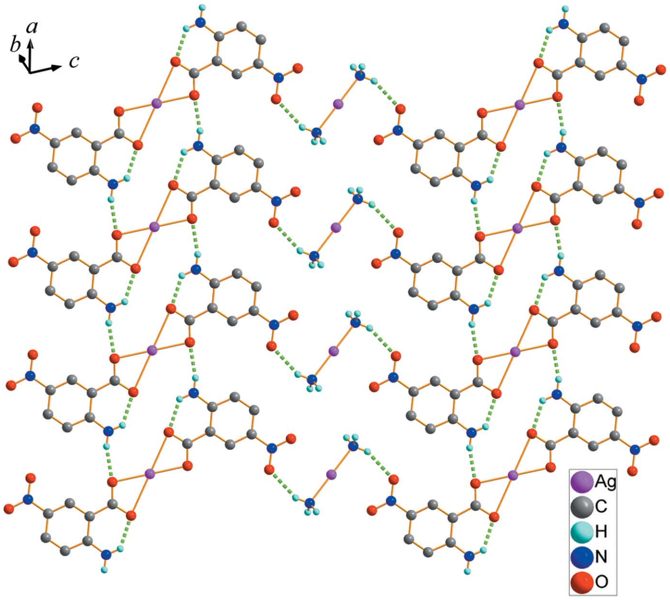


Figure 2
A perspective view of the two-dimensional supramolecular sheet of (I), incorporating intra- and intermolecular N—H⋯O hydrogen bonds (dashed lines).

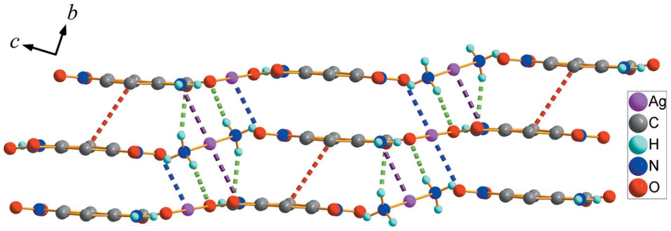


Figure 3
A perspective view of the three-dimensional supramolecular framework of (I), showing intersheet hydrogen bonds and Ag⋯O, Ag⋯N and π–π interactions as dashed lines. (In the electronic version of the paper, these dashed lines are green, blue, purple and red, respectively.)

ion (Ag1) adopts a linear coordination environment, coordinated by two symmetry-related ammonia molecules to form the $[Ag(NH_3)_2]^+$ cation. The Ag1—N3 bond length is 2.1193 (16) Å, which is comparable with the corresponding values observed in another silver(I)–ammonia complex (You & Zhu, 2004). The other Ag^I ion (Ag2) is located in a rare four-coordination planar environment (only ~2% of all reported silver complexes possess this stereochemistry (Young & Hanton, 2008), which is completed by two chelating inversion-related anbz ligands. This geometry is not a perfect square-planar arrangement, but is distorted due to the acute bite angle [53.02 (4)°] and differing Ag—O bond lengths (Table 1), both of which are imposed by the asymmetrically chelated ring.

There are abundant weak interactions around Ag1 and Ag2. Ag1⋯O2 and Ag1⋯N1^i [3.1195 (15) and 3.1885 (16) Å, respectively; symmetry code: (i) $x + 1$, y, $z - 1$] are slightly shorter than the sums of the van der Waals radii of Ag and O (3.24 Å) and Ag and N (3.27 Å) (Bondi, 1964). The Ag2⋯O2^{ii} interaction [symmetry code: (ii) $-x + 2$, $-y + 1$, $-z + 1$] is along the axial direction above and below the AgO_4 plane. A possible reason for the four-coordinate planar geometry may be the steric shielding of axial sites by the nitro groups (Reger *et al.*, 2004).

The anionic and cationic parts of (I) interact with each other to form a one-dimensional zigzag chain through weak Ag⋯O_{nitro} interactions, alternating with interionic N3—H3*B*⋯O1 hydrogen bonds (Table 2) to give a $C_2^2(6)$ chain-like motif (Bernstein *et al.*, 1995). Additionally, intra-anion N1—H1*C*⋯O4 hydrogen bonds, showing an *S*(6) motif, consolidate the one-dimensional chains, which are further linked into a slightly undulating two-dimensional supramolecular sheet (Fig. 2) *via* intermolecular N1—H1*B*⋯O3^v hydrogen bonds [symmetry code: (v) $x - 1$, y, z]. The intersheet distance is *ca* 3.3 Å, which is comparable with those of graphite and Ag_6(benzene-1,3,5-tricarboxylic acid)$_2$(2-aminopyrazine)$_6$ (Sun, Luo, Xu *et al.* 2009), and is a result of the fact that there are no axial ligands perpendicular to the two-dimensional sheets.

The shortest centroid–centroid distance between parallel benzene rings of the anbz ligands is 3.8523 (9) Å, with a large slippage of 2.065 Å, which suggests the existence of weak offset face-to-face π–π stacking interactions. These combine with the inter-sheet ammine–nitro N—H⋯O [mean N⋯O distance = 3.131 (2) Å] hydrogen bonds and Ag⋯O_{nitro} and Ag⋯N_{amino} interactions to stabilize the resultant three-dimensional supramolecular framework (Fig. 3).

Experimental

All reagents and solvents were obtained commercially and used without further purification. A mixture of Ag_2O (116 mg, 0.5 mmol) and H_2anbz (182 mg, 1 mmol) was stirred in a methanol–H_2O mixed solvent (10 ml, 1:1 *v*/*v*). An aqueous NH_3 solution (25%, 0.5 ml) was then added dropwise to the mixture to give a clear solution under ultrasonic treatment. The resulting solution was allowed to evaporate slowly in the dark at room temperature for several days to give colourless crystals of (I), which were washed with a small volume of cold ethanol and diethyl ether (yield 61%, based on Ag_2O). Analysis calculated for $C_{14}H_{16}Ag_2N_6O_8$: C 27.47, H 2.63, N 13.73%; found: C 27.51, H 2.59, N 13.64%.

Crystal data

$[Ag(NH_3)_2][Ag(C_7H_5N_2O_4)_2]$
$M_r = 612.07$
Triclinic, $P\overline{1}$
$a = 7.1361$ (5) Å
$b = 7.4070$ (6) Å
$c = 9.9686$ (6) Å
$\alpha = 87.064$ (6)°
$\beta = 79.170$ (6)°
$\gamma = 62.077$ (8)°
$V = 456.86$ (6) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 2.20$ mm^{-1}
$T = 173$ K
0.10 × 0.10 × 0.08 mm

Data collection

Oxford Xcalibur diffractometer with a Sapphire3 Gemini Ultra detector
Absorption correction: multi-scan [*CrysAlis Pro* (Oxford Diffraction, 2009); empirical (using intensity measurements) absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm]
$T_{min} = 0.810$, $T_{max} = 0.843$
3721 measured reflections
1800 independent reflections
1627 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$

Acta Cryst. (2010). C**66**, m174–m176 Sun *et al.* • $[Ag(NH_3)_2][Ag(C_7H_5N_2O_4)_2]$ **m175**

Table 1
Selected geometric parameters (Å, °).

Ag1—N3	2.1193 (16)	Ag2—O3	2.2367 (12)
Ag1—O2	3.1195 (15)	Ag2—O4	2.6541 (13)
Ag1—N1^{i}	3.1885 (16)	Ag2—O2^{ii}	2.9287 (15)

N3^{iii}—Ag1—O2	86.84 (5)	O3—Ag2—O4	53.02 (4)
N3—Ag1—O2	93.16 (5)	O3^{iv}—Ag2—O4	126.98 (4)
N3^{iii}—Ag1—N1^{i}	94.79 (5)	O3—Ag2—O2^{ii}	74.82 (4)
N3—Ag1—N1^{i}	85.21 (5)	O3^{iv}—Ag2—O2^{ii}	105.18 (4)
O2—Ag1—N1^{i}	108.73 (4)	O4—Ag2—O2^{ii}	88.11 (4)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O3^{v}	0.88	2.09	2.9473 (18)	164
N1—H1*C*···O4	0.88	2.03	2.685 (2)	131
N3—H3*D*···O3^{vi}	0.91	2.37	3.185 (2)	149
N3—H3*C*···O4^{i}	0.91	2.21	3.077 (2)	159
N3—H3*B*···O1	0.91	2.29	3.038 (2)	139

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.048$
$S = 1.07$
1800 reflections
140 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.47$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}

All H atoms were placed in calculated positions and refined using a riding model, with aromatic C—H = 0.95 Å, amino N—H = 0.88 Å and ammine N—H = 0.91 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C or N)].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; 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: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3131). Services for accessing these data are described at the back of the journal.

References

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Blake, A. J., Brooks, N. R., Champness, N. R., Cooke, P. A., Deveson, A. M., Fenske, D., Hubberstey, P., Li, W. S. & Schröder, M. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2103–2110.

Blake, A. J., Champness, N. R., Hubberstey, P., Li, W.-S., Withersby, M. A. & Schröder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.

Blake, A. J., Hill, S. J., Hubberstey, P. & Li, W. S. (1997). *J. Chem. Soc. Dalton Trans.* pp. 913–914.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–452.

Brandenburg, K. (2008). *DIAMOND*. Version 3.1f. Crystal Impact GbR, Bonn, Germany.

Fritchie, C. J. Jr (1972). *J. Biol. Chem.* **247**, 7459–7464.

Oxford Diffraction (2008). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.32.24. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

Oxford Diffraction (2009). *CrysAlis Pro*. Version 1.171.33.46. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

Pajunen, A. & Pajunen, S. (1994). *Acta Cryst.* C**50**, 1884–1886.

Paul, B., Nather, C., Fromm, K. M. & Janiak, C. (2005). *CrystEngComm*, **7**, 309–319.

Reger, D. L., Gardinier, J. R. & Smith, M. D. (2004). *Polyhedron*, **23**, 291–299.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sun, D., Luo, G.-G., Huang, R.-B., Zhang, N. & Zheng, L.-S. (2009). *Acta Cryst.* C**65**, m305–m307.

Sun, D., Luo, G.-G., Xu, Q.-J., Zhang, N., Jin, Y. C., Zhao, H. X., Lin, L.-R., Huang, R.-B. & Zheng, L.-S. (2009). *Inorg. Chem. Commun.* **12**, 782–784.

Sun, D., Luo, G.-G., Zhang, N., Xu, Q.-J., Huang, R.-B. & Zheng, L.-S. (2010). *Polyhedron*, **29**, 1243–1250.

Sun, D., Zhang, N., Luo, G.-G., Xu, Q.-J., Huang, R.-B. & Zheng, L.-S. (2010). *Polyhedron*, **29**, 1842–1848.

Sun, D., Zhang, N., Xu, Q.-J., Huang, R.-B. & Zheng, L.-S. (2010). *J. Organomet. Chem.* **695**, 1598–1602.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

Whitcomb, D. R. & Rajeswaran, M. (2008). *Inorg. Chim. Acta*, **361**, 1357–1362.

Yaghi, O. M., O'Keeffe, M., Ockwig, N. W., Chae, H. K., Eddaoudi, M. & Kim, J. (2003). *Nature (London)*, **423**, 705–714.

You, Z.-L. & Zhu, H.-L. (2004). *Acta Cryst.* C**60**, m517–m519.

You, Z.-L., Zhu, H.-L. & Liu, W.-S. (2004). *Acta Cryst.* E**60**, m1624–m1626.

Young, A. G. & Hanton, L. R. (2008). *Coord. Chem. Rev.* **252**, 1346–1386.

Zheng, G. L., Li, Y. Y., Deng, R. P., Song, S. Y. & Zhang, H. J. (2008). *CrystEngComm*, **10**, 658–660.

Zheng, S. L., Tong, M. L., Chen, X. M. & Ng, S. W. (2002). *J. Chem. Soc. Dalton Trans.* pp. 360–364.

Zheng, S. L., Volkov, A. C., Nygren, L. & Coppens, P. (2007). *Chem. Eur. J.* **13**, 8583–8590.

m176 Sun *et al.* • $[Ag(NH_3)_2][Ag(C_7H_5N_2O_4)_2]$ *Acta Cryst.* (2010). C**66**, m174–m176