

A silver(I) complex with Ag⁺··Ag interactions:
diamminesilver(I) *p*-nitrobenzoateZhong-Lu You,^{a,b} Hai-Liang
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Key indicators

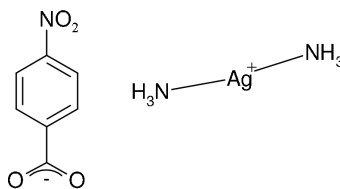
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
R factor = 0.042
wR factor = 0.094
Data-to-parameter ratio = 14.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $[\text{Ag}(\text{NH}_3)_2](\text{C}_7\text{H}_4\text{NO}_4)$, is a mononuclear silver(I) complex with two cations and two anions in the asymmetric unit. The cations have almost linear coordination geometry with two ammine ligands and are linked into centrosymmetric pairs by weak Ag⁺··Ag interactions. In the crystal structure, the cations and anions are linked together through N—H···O hydrogen bonds, forming a three-dimensional structure.

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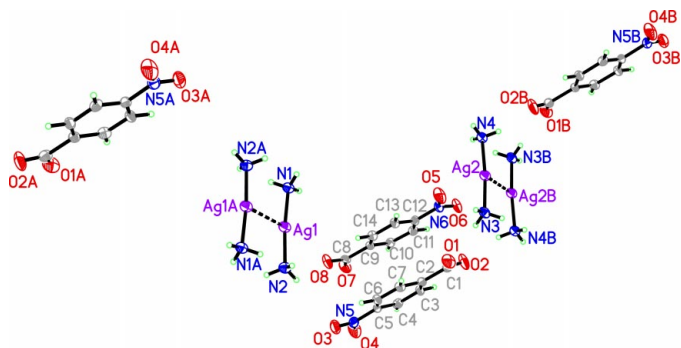
Comment

Ag^I complexes with carboxylate anions as counter-ions or ligands are a group of metal compounds that, because of their wide usage in many fields, have been structurally characterized for many years (Smith *et al.*, 1996; Kristiansson, 2001; Nomiya *et al.*, 2000; Wei *et al.*, 1998; Zheng *et al.*, 2001). Studying the variety of products in the self-assembly processes between labile metal ions and flexible multidentate ligands is an interesting topic in supramolecular chemistry. The balance between the formation of different structures is often subtle. Factors that affect the coordination topology include not only the highly influential factors of metal and ligand coordination preferences but also anion-based influences. The latter factor is particularly notable in Ag^I coordination complexes (Erxleben, 2001; Khlobystov *et al.*, 2001). Owing to the versatile coordination geometry of Ag^I, coordination numbers from two to six are possible, and because of the relatively weak nature of many Ag^I–ligand interactions, including some anion–Ag interactions, such compounds are particularly

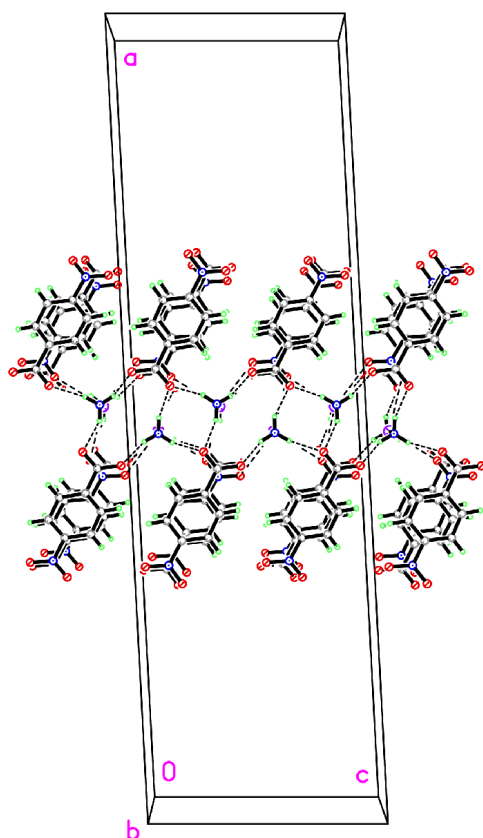


(I)

susceptible to the influence of weaker supramolecular forces. However, the different nucleophilicities and sizes of the anions must be a significant factor in generating the different molecular structures. More work needs to be done to understand better the controlling effect of anions; this is now becoming an interesting topic in supramolecular chemistry (Cai *et al.*, 2002; Xu *et al.*, 2001). Recently, we have reported a few silver(I) complexes (You, Zhu & Liu, 2004; You, Yang *et al.*, 2004). As an extension of our work on the structural characterization of silver(I) complexes, the title complex, (I), is reported here.


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix 'A' are at the symmetry position $(-x, -y, 2-z)$, while those labelled with the suffix 'B' are at the symmetry position $(\frac{1}{2}-x, \frac{3}{2}-y, 1-z)$. Dashed lines indicate the weak interactions between Ag atoms.


Figure 2

Part of the crystal packing of (I), viewed along the *b* axis. Dashed lines indicate intermolecular hydrogen bonds.

Compound (I) is a mononuclear silver(I) complex with two cations and two anions in the asymmetric unit. The anions are related by a pseudo-inversion centre at (0.125, 0.376, 0.248) and have slightly different orientations of the nitro and carboxylate groups. Each Ag^I atom is in a linear coordination environment, coordinated by two ammonia molecules. The average Ag–N bond length [2.114 (6) Å; Table 1] is comparable to the corresponding values observed in other silver(I) complexes (You & Zhu, 2004). All other bond lengths are in normal ranges (Allen *et al.*, 1987). The N1–Ag1–N2

[174.62 (19)°] and N3–Ag2–N4 [172.70 (18)°] angles deviate from the ideal 180°, as a result of weak interactions between the Ag atoms. The Ag1ⁱ···Ag1ⁱ [symmetry code: (i) $-x, -y, 2-z$] and Ag2ⁱⁱ···Ag2ⁱⁱ [symmetry code: (ii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$] distances [3.308 (3) and 3.149 (3) Å, respectively] are shorter than the sum of the van der Waals radii of two Ag atoms [3.44 Å] and are comparable to the value of 3.035 (2) Å observed in another silver complex with weak Ag···Ag interactions (Zhu *et al.*, 2003), indicating the existence of weak ligand-unsupported metal–metal interactions in (I). These interactions link the cations into centrosymmetric dimers.

In the crystal structure, the cations and anions are linked together through intermolecular N–H···O hydrogen bonds, forming a three-dimensional structure (Table 2 and Fig. 2).

Experimental

Ag₂O (0.1 mmol, 23.2 mg) and 4-nitrobenzoic acid (0.2 mmol, 33.2 mg) were dissolved in a 30% aqueous ammonia solution (10 ml) and stirred for *ca* 15 min to give a clear colourless solution. The solution was kept in the dark at room temperature for 5 d. Colourless block-shaped crystals of (I) formed after slow evaporation of the solvent. The crystals were isolated, washed three times with water and dried in a vacuum desiccator using anhydrous CaCl₂ (yield 81.2%). Analysis found: C 27.1, H 3.3, N 13.7%; calculated for C₇H₁₀AgN₃O₄: C 27.3, H 3.3, N 13.6%.

Crystal data

[Ag(NH₃)₂](C₇H₄NO₄)
M_r = 308.05
 Monoclinic, *C*2/*c*
a = 42.152 (8) Å
b = 7.643 (2) Å
c = 12.435 (2) Å
 β = 93.03 (3)°
V = 4000.6 (14) Å³
Z = 16

D_x = 2.046 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1872 reflections
 θ = 1.7–25.4°
 μ = 2.01 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.33 × 0.28 × 0.23 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.534, *T_{max}* = 0.635
 8989 measured reflections

4063 independent reflections
 2241 reflections with *I* > 2σ(*I*)
R_{int} = 0.059
 θ_{max} = 26.5°
h = -52 → 27
k = -9 → 9
l = -15 → 13

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.042
wR (*F*²) = 0.094
S = 0.88
 4063 reflections
 275 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0361P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.83 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{min} = -0.58 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ag1–N2	2.103 (6)	Ag2–N4	2.115 (6)
Ag1–N1	2.121 (6)	Ag2–N3	2.116 (6)
Ag1 ⁱ ···Ag1 ⁱ	3.308 (3)	Ag2 ⁱⁱ ···Ag2 ⁱⁱ	3.149 (3)
N2–Ag1–N1	174.62 (19)	N4–Ag2–N3	172.70 (18)

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H4C...O6 ⁱⁱⁱ	0.89	2.37	3.165 (7)	149
N4—H4B...O2 ⁱⁱ	0.89	2.13	2.994 (7)	164
N4—H4D...O1 ^{iv}	0.89	2.15	3.002 (7)	161
N3—H3C...O1	0.89	2.20	2.992 (7)	148
N3—H3B...O2 ^v	0.89	2.44	3.241 (9)	150
N3—H3D...O6 ^{vi}	0.89	2.38	3.254 (7)	165
N2—H2C...O7 ^{viii}	0.89	2.20	3.030 (7)	155
N2—H2B...O8 ^{viii}	0.89	2.19	3.047 (7)	160
N2—H2A...O8 ^{ix}	0.89	2.22	3.045 (7)	154
N1—H1C...O8 ^{vi}	0.89	2.41	3.250 (7)	157
N1—H1B...O8 ^x	0.89	2.35	3.152 (8)	150
N1—H1A...O7 ^{xi}	0.89	2.17	2.995 (7)	154

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

All H atoms were found in a difference map and then placed in idealized positions and constrained to ride on their parent atoms, with N—H and C—H distances of 0.89 and 0.96 Å, respectively. The $U_{\text{iso}}(\text{H})$ values were set at $1.5U_{\text{eq}}(\text{N})$ for amine H atoms and fixed at 0.08 \AA^2 for other H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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