Bis(dibenzylamine)silver(I) nitrate

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The crystal structure of the title compound, [Ag-(C$_{14}$H$_{15}$N)$_2$]NO$_3$, is the first reported structure of a silver complex with the dibenzylamine ligand. In the cation, the Ag^{I} atom is linearly coordinated by two N atoms from dibenzylamine ligands, with Ag—N distances of 2.173 (3) and 2.178 (3) Å, and an N—Ag—N angle of 168.44 (10)°.

Comment

The title compound, (I), was formed by accident, instead of the expected sulfenamide. A search in the Cambridge Structural Database (Version 5.26; Allen, 2002) for coordination compounds with dibenzylamine yielded only ten structures, namely chloro(dibenzylamine-*N*)dimethylaluminium(III) (Craig *et al.*, 1998), bis(dibenzylamine-*N*)bis(*N*,*N*-dibenzyl-carbamato-*O*)copper (II) (Dell'Amico *et al.*, 2002), (μ_2-dibenzylamido)dibenzylaminetrimethylaluminiumlithium (Armstrong *et al.*, 1996), dibenzylaminotrimethylaluminium (Armstrong *et al.*, 1996), bis[(μ_2-tetrahydridoborate-*H*,*H*,*H'*,*H'*)bis(dibenzylamino)lithium] (Giese *et al.*, 2001), dibenzylaminotrimethylgallium (Lake *et al.*, 1999), dibenzyl-aminotrimethylindium (Lake *et al.*, 1999), bis(dibenzyl-amine)bis(ethylthioacetato)copper(II) (Sato & Ouchi, 1982), *catena*-bis(dibenzylamine-*N*)bis(μ_2-thiocyanato-*S*,*N*)cadmium(II) (Taniguchi & Ouchi, 1987) and trichloro-bis(dibenzylamino)indium (Pauls *et al.*, 2001). Here, we present the crystal structure of the title compound, (I). To our knowledge, this is the first crystal structure of a silver complex with the dibenzylamine ligand.

(I)
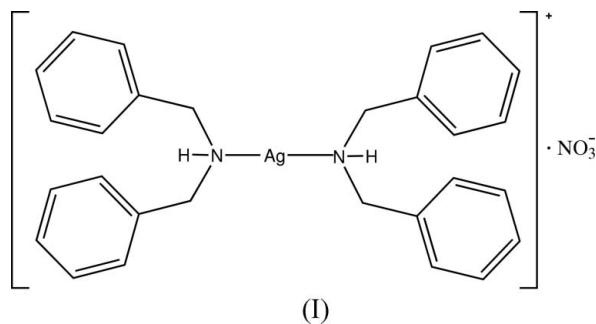
The Ag atom in (I) (Fig. 1) is linearly coordinated by the N atoms of two dibenzylamine molecules, with Ag—N distances of 2.173 (3) and 2.178 (3) Å. These values are shorter than those found in other linear silver complexes where Ag is bonded to amine groups. A representative example is bis[μ_2-2-(diphenylphosphino)aniline]gold(I)silver(I) bis(trifluoro-methanesulfonate) dichloromethane solvate, with a mean Ag—N distance of 2.253 (8) Å (Crespo *et al.*, 2002). The
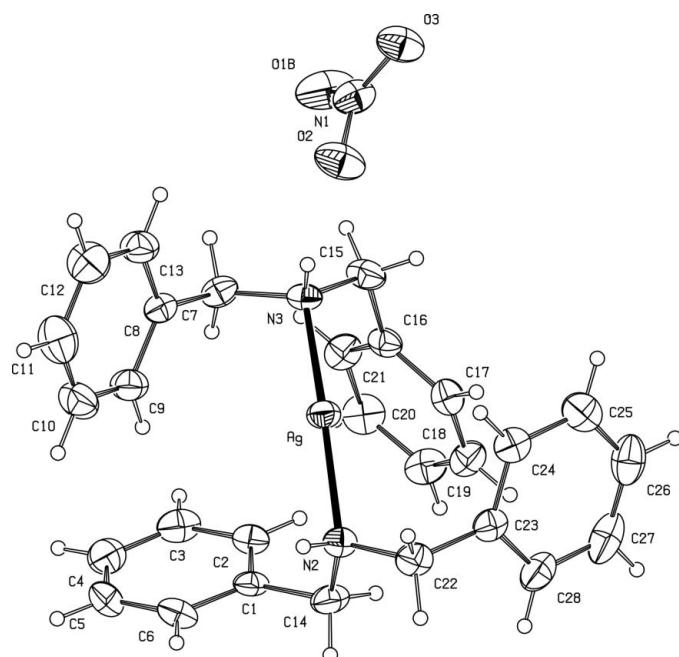
Figure 1
A view of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Only the major component (O1*B*) of the disordered O atom is shown.

molecular dimensions in the complex cation of (I) (Table 1) are within normal ranges (Allen *et al.*, 1987), with the following mean bond distances: Csp^3—Csp^2 = 1.503 (5), Csp^2—Csp^2 = 1.376 (6) and Csp^3—N = 1.481 (5) Å. The nitrate anion has normal geometric parameters. The dihedral angles between phenyl rings C1–C6 and C8–C13, C1–C6 and C16–C21, C1–C6 and C23–C28, C8–C13 and C16–C21, C8–C13 and C23–C28, and C16–C21 and C23–C28 are 90.5 (1), 101.1 (1), 94.1 (1), 97.2 (1), 161.2 (1) and 99.8 (1)°, respectively.

The crystal packing of (I) (Fig. 2) is stabilized by intermolecular N—H···O and C—H···O hydrogen bonds (Table 2). The relatively short H9···*Cg*1 and H2···*Cg*2 (*Cg*1 is the centroid of the C1–C6 ring and *Cg*2 is the centroid of the C16–C21 ring) distances of 2.74 and 2.71 Å, respectively, indicate possible intramolecular C—H···π interactions, which contribute to the stability of the crystal structure.

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled prior to use. The title compound was obtained as colourless prismatic crystals, in an attempt to prepare a sulfenamide by the known metal-assisted technique (Davis *et al.*, 1977). Into a 1000 ml three-necked flask equipped with an overhead stirrer was placed silver nitrate (7.8 g, 0.045 mol) in methanol (400 ml). After dissolution had taken place, an equivalent amount of bis(4-*tert*-butyl-1-isopropyl-2-imidazolyl)disulfide was added and the reaction mixture cooled in an ice bath. An excess of dibenzylamine (5 equivalents) was added and the reaction mixture stirred overnight. The silver mercaptide which formed was filtered off and the solvent removed at reduced pressure, at a temperature of 308–313 K. The resulting residue was dissolved in diethyl ether,
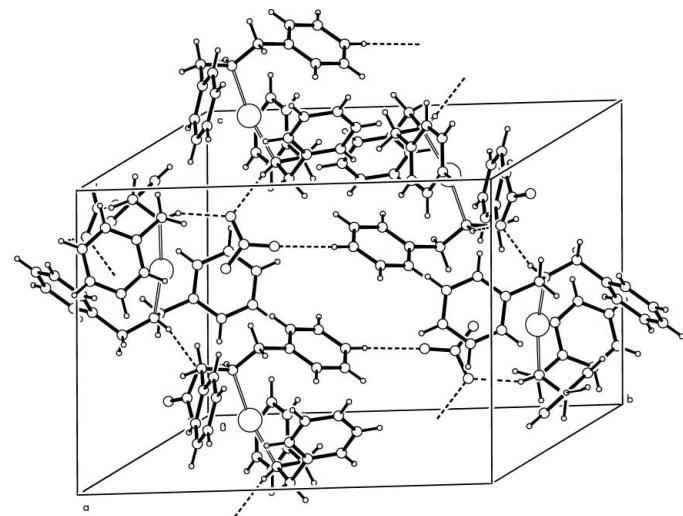

Figure 2
The crystal packing of (I), with intermolecular hydrogen bonds shown by dashed lines.

washed with water (4 × 100 ml) and dried over MgSO$_4$. The compound was crystallized from methanol–water, collected by filtration and dried in a vacuum desiccator over CaCl$_2$. Colourless prismatic crystals of (I) suitable for X-ray analysis were grown from a methanol–water solution (1:1 *v/v*) at 298 K over a period of a few days. FT–IR (KBr, *v*, cm^{-1}): 3151 (*vw*), 3060 (*w*), 3023 (*w*), 2930 (*w*), 2357 (*m*), 2341 (*m*), 1491 (*m*), 1449 (*w*), 1381 (*vs*), 1050 (*w*), 821 (*w*), 739 (*m*), 694 (*s*), 570 (*w*), 470 (*w*), 496 (*w*), 490 (*w*), 455 (*w*), 403 (*w*).

Crystal data

[Ag(C$_{14}$H$_{15}$N)$_2$]NO$_3$	D_x = 1.433 Mg m^{-3}
M_r = 564.42	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 6703
a = 12.034 (4) Å	reflections
b = 18.672 (8) Å	θ = 1.8–28.7°
c = 12.218 (5) Å	μ = 0.80 mm^{-1}
β = 107.67 (3)°	T = 298 (2) K
V = 2615.8 (18) Å^3	Prism, colourless
Z = 4	0.35 × 0.23 × 0.19 mm

Data collection

Nonius KappaCCD area-detector diffractometer	5979 independent reflections
	4939 reflections with $I > 2\sigma(I)$
φ scans, and ω scans with κ offsets	R_{int} = 0.057
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	θ_{max} = 27.5°
	h = −15 → 13
T_{min} = 0.798, T_{max} = 0.858	k = −24 → 22
21322 measured reflections	l = −12 → 15

Refinement

Refinement on F^2	w = 1/[$\sigma^2(F_o^2)$ + (0.0346P)^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046	+ 1.8327P]
$wR(F^2)$ = 0.102	where P = (F_o^2 + 2F_c^2)/3
S = 1.13	$(\Delta/\sigma)_{max}$ = 0.03
5979 reflections	$\Delta\rho_{max}$ = 0.51 e Å^{-3}
330 parameters	$\Delta\rho_{min}$ = −0.44 e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

metal-organic papers

Table 1
Selected geometric parameters (Å, °).

Ag—N3	2.173 (3)	N3—C15	1.488 (4)
Ag—N2	2.178 (3)	C1—C14	1.508 (4)
N2—C14	1.474 (4)	C7—C8	1.497 (4)
N2—C22	1.481 (4)	C15—C16	1.499 (4)
N3—C7	1.481 (4)	C22—C23	1.505 (5)
N3—Ag—N2	168.44 (10)	C7—N3—C15	112.6 (3)
C14—N2—C22	112.6 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H29$\cdots$O2^i	0.78 (4)	2.17 (4)	2.933 (4)	166 (4)
N2—H30$\cdots$O2	0.81 (4)	2.12 (4)	2.863 (4)	153 (3)
C4—H4$\cdots$O1B^{ii}	0.93	2.57	3.475 (7)	165

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

The disordered atom O1 was refined with a split model over two positions, with occupancies of 0.073 (2) and 0.927 (2) for O1A and O1B, respectively. C-bound H atoms were positioned gemetrically and refined as riding, with $C_{aromatic}$—H = 0.93 Å and $C_{methylene}$—H = 0.97 Å, and with U_{iso}(H) = 1.2U_{eq}(C). Atoms H29 and H30, attached to N2 and N3, respectively, were located in a difference Fourier map and refined freely, with U_{iso}(H) = 1.2U_{eq}(N).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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