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Bis[2-(phenylazo)imidazole-*N*]silver(I) nitrate methanol solvate

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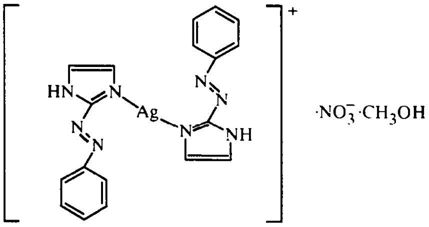
Abstract

The title compound, bis(2-phenyldiazenyl-1*H*-imidazole-*N*)silver(I) nitrate methanol solvate, $[Ag(C_9H_8N_4)_2]NO_3\cdot CH_3OH$, is a monomeric complex linearly coordinated by two N atoms from two different imidazole rings, with Ag—N bond distances of 2.138 (3) and 2.147 (3) Å, and an N—Ag—N bond angle of 174.9 (1)°. The crystal packing is stabilized by weak intramolecular N—H···O and O—H···O hydrogen bonds and an intermolecular N—H···O hydrogen bond involving the nitrate anion and the methanol solvent.

Comment

Recently, the design of molecular architectures with imidazole has aroused interest because of their role in understanding biomolecular interactions with metal ions and in providing models for the active sites of metalloproteins. Ligands consisting of one imidazole ring as a pendant nitrogen donor from an azo function have been employed in the development of ruthenium(II) coordination chemistry, due to the unsymmetric *N*-donor sites in the azo–imine –N=N—C=N– function (Misra *et al.*, 1998). In this paper, we report the crystal structure of a silver complex of (2-phenylazo)imidazole, (I).



(I)

The molecular structure and atom-numbering scheme of (I) are shown in Fig. 1. The phenylazo group

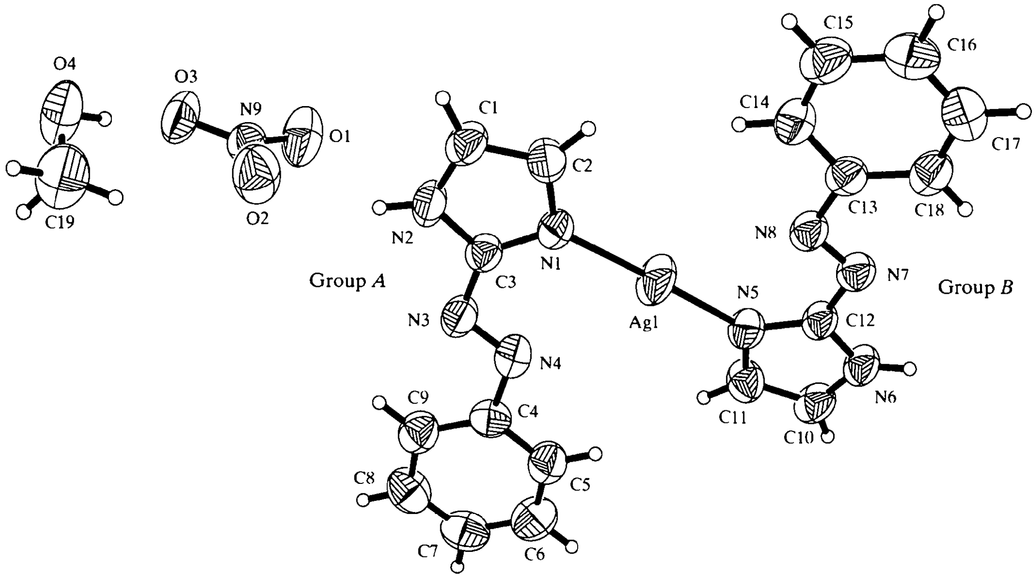


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

is in the *E* configuration. The N3—C3, N4—C4, N7—C12 and N8—C13 bond distances are comparable with the average value of 1.437 Å in other *E*-azo compounds. The N═N distances [N3═N4 = 1.229 (5) and N7═N8 = 1.250 (5) Å] are quite normal, as are the C—N═N angles of 111.9 (3), 113.7 (3), 113.3 (3) and 114.2 (3)°, although the N═N distances in (I) are comparatively shorter than those in $C_{28}H_{34}Cl_2N_8Ru$ [N3═N4 = 1.299 (5) Å] and in $C_{22}H_{24}Cl_2N_8Ru$ [N3═N4 = 1.307 (5) Å and N7═N8 = 1.301 (5) Å] (Misra *et al.*, 1998). The Ag—N bond distances are 2.138 (3) and 2.147 (3) Å, and these values are comparable to those of 2.12 and 2.13 Å in $Ag(C_3H_4N_2)_2NO_3$ (Antti *et al.*, 1971).

The inclination between the imidazole and phenyl rings of the two (2-phenylazo)imidazole groups, *A* and *B*, is 5.7 (3) and 4.9 (3)°, respectively. Such relatively low values show the planarity of the molecules. In addition, the two (2-phenylazo)imidazole groups (*A* and *B*) have a dihedral angle of 14.3 (3)° between them. The Ag atom deviates by 0.342 (1) and 0.345 Å from the planes of *A* and *B*, respectively. The distances of the Ag atom from the centroids of the phenyl rings of *A* ($-x, -y, -z$) and *B* ($-x-1, -y, 1-z$) (3.685 and 3.667 Å, respectively) show that the conformation is the same for the two groups. Groups *A* and *B* are tilted through 39° with respect to each other, as can be seen from the N5—Ag1—N1—C3 and N1—Ag1—N5—C11 torsion angles of 39 (1) and −39 (2)°, respectively.

The title complex is monomeric and the Ag atom is not in the expected four-coordinate environment, but is linked to only two N atoms from different imidazole rings in a linear coordination [N1—Ag1—N5 = 174.9 (1)°]. This is comparable to the values in $[Ag(NO_3)(H_2biim)]_n$ [biim is biimidazole; N1*B*—Ag—N2*A* = 162.3 (1)°; Hester *et al.*, 1997] and $Ag(C_3H_4N_2)_2NO_3$ (N11—Ag—N21 = 172.0°; Antti *et al.*, 1971).

The presence of the methanol solvent and the nitrate group in the molecule enhances the crystal packing through intra- and intermolecular hydrogen bonds (Table 2), which result in the formation of an infinite chain running along [1$\bar{1}$1].

Experimental

The title compound was prepared by adding a methanolic solution of (2-phenylazo)imidazole (Fargher & Pyman, 1919) to a stirred methanolic solution of $AgNO_3$ at 323 K to give a clear mixture. After several days of slow evaporation at room temperature, orange single crystals of (I) were obtained.

Crystal data

$[Ag(C_9H_8N_4)_2]NO_3{\cdot}CH_4O$
$M_r = 546.31$
Triclinic
$P\bar{1}$
$a = 7.5447$ (5) Å
$b = 12.0046$ (7) Å
$c = 13.7852$ (8) Å
$\alpha = 74.077$ (1)°
$\beta = 75.359$ (1)°
$\gamma = 72.462$ (1)°
$V = 1124.96$ (12) Å^3
$Z = 2$
$D_x = 1.613$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4099 reflections
$\theta = 1.56$–28.31°
$\mu = 0.942$ mm^{-1}
$T = 293$ (2) K
Slab
0.30 × 0.20 × 0.14 mm
Orange

Data collection

Siemens SMART CCD area detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.765$, $T_{max} = 0.879$
7937 measured reflections
5431 independent reflections
3463 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 28.29°$
$h = -9 \rightarrow 10$
$k = -13 \rightarrow 16$
$l = -15 \rightarrow 18$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.160$
$S = 1.013$
5431 reflections
314 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.2004P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.477$ e Å^{-3}
$\Delta\rho_{min} = -0.561$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ag1—N5	2.138 (3)	O4—C19	1.382 (8)
Ag1—N1	2.147 (3)	N3—N4	1.229 (5)
O1—N9	1.236 (5)	N7—N8	1.250 (5)
O2—N9	1.226 (5)	N7—C12	1.390 (5)
O3—N9	1.245 (4)	N8—C13	1.438 (6)
N5—Ag1—N1	174.9 (1)	N7—N8—C13	114.2 (3)
N4—N3—C3	111.9 (3)	O2—N9—O1	119.4 (4)
N3—N4—C4	113.7 (3)	O2—N9—O3	120.5 (4)
N8—N7—C12	113.3 (3)	O1—N9—O3	120.1 (4)
C3—N3—N4—C4	−178.9 (3)	C12—N7—N8—C13	−179.7 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O2	0.86	2.148	2.939 (5)	153
O4—H1O4···O3	0.94 (8)	1.83 (8)	2.767 (6)	172 (7)
N6—H6*A*···O4^i	0.86	1.857	2.702 (6)	167

Symmetry code: (i) $1 + x, y - 1, 1 + z$.

The H atoms of the methanol solvate were refined. The maximum electron density of 1.477 e Å^{-3} is located at a distance of 1 Å from the Ag atom.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1302). Services for accessing these data are described at the back of the journal.

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Dibromo[propane-1,3-diylbis(diphenylphosphine)-*P*,*P*′]palladium(II)

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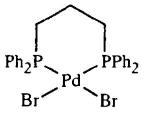
Abstract

In the title compound, *cis*-$[PdBr_2\{Ph_2P(CH_2)_3PPh_2\}]$, the Pd atom is coordinated to the diphosphine ligand through the P atoms and to two bromo ligands in a slightly distorted square-planar arrangement. The displacements of the P atoms from the $PdBr_2$ plane are 0.066 and −0.349 Å, a consequence of the steric strain caused by the eclipsing of bonds in the alkyl chain of the phosphine.

Comment

It is well known that palladium(II) frequently forms square-planar complexes in which the metal centre is coordinated to two P atoms of tertiary phosphine ligands and to two mutually *cis* halide ligands. Many crystal structures have been reported in which the halogen is chlorine, but to the best of our knowledge, only three structures of this type are known with bromine (Wilson *et al.*, 1996; Peters *et al.*, 1984).

The crystal structure of the title complex, (I), consists of equivalent discrete *cis*-$[PdBr_2\{Ph_2P(CH_2)_3PPh_2\}]$ molecules. The coordination around palladium is slightly distorted square planar, with the most noticeable distortion in the P2—Pd1—Br2 angle of 88.04 (5)°. The remaining angles around palladium are closer to the ideal value of 90° for a square-planar geometry and the sum of the angles about the metal centre is 360.28°. The planar coordination is slightly distorted, with displacements of the P atoms from the $PdBr_2$ plane of 0.066 (P1) and −0.349 Å (P2). This is probably a consequence of the steric strain caused by the appreciable eclipsing of bonds in the alkyl chain of the phosphine required if both P atoms are to bond to the same Pd atom. The strain is also indicated in the bond angles in the alkyl chain,



(I)

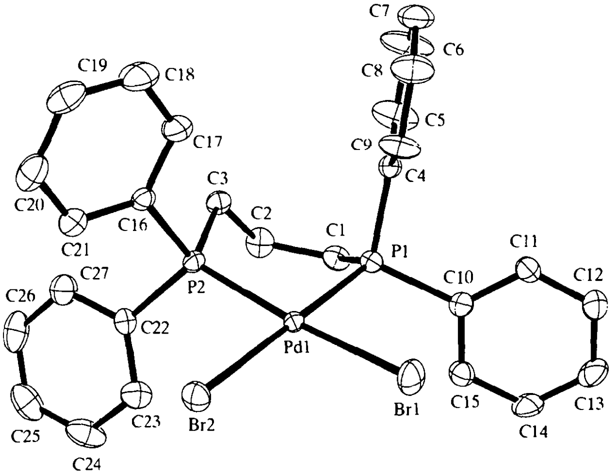


Fig. 1. View of the title compound with 30% probability displacement ellipsoids. H atoms have been omitted for clarity.