

Bis(3,5-dimethylpyrazole- κN^2)silver(I) nitrate

Ahmed A. Mohamed and John P. Fackler Jr*

Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, PO Box 30012, College Station, Texas 77842-3012, USA

Correspondence e-mail: fackler@mail.chem.tamu.edu

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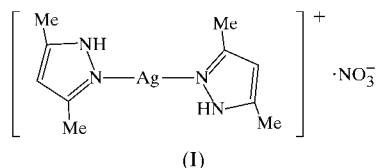
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The two independent bis(3,5-dimethylpyrazole)silver(I) cations in crystalline $[\text{Ag}(\text{C}_5\text{H}_7\text{N}_2)_2]\text{NO}_3$ display N—Ag—N angles of 175.51 (14) and 174.44 (13)°, and an average Ag—N distance of 2.124 (5) Å. The nitrate anion is situated between $[\text{Ag}(\text{C}_5\text{H}_7\text{N}_2)_2]^+$ units and interacts *via* hydrogen bonds with the NH groups. The two 3,5-dimethylpyrazole ligands are *trans* about the silver center. Only a small deviation from linearity is observed in the coordination around silver.

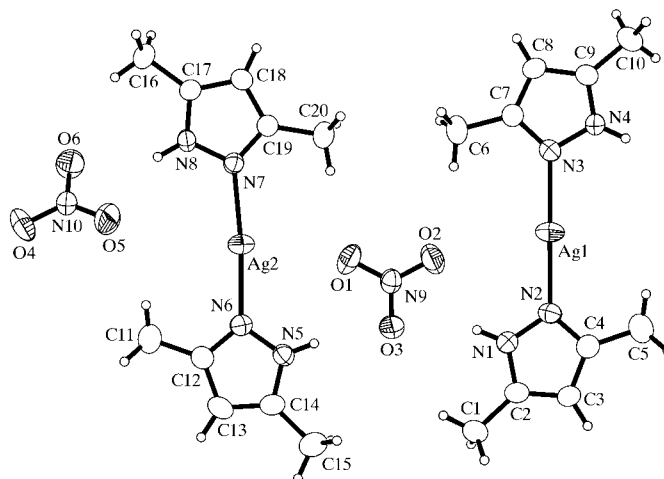
Comment

The chemistry of pyrazole and pyrazolate–metal complexes is quite extensive (Trofimenko, 1972, 1986). There has been much interest in the chemistry of pyrazolate adducts of coinage (group 11) metals (La Monica & Ardizzoia, 1997).

In recent years, we have been investigating the coordination chemistry of Ag^{I} , Au^{I} , and Cu^{II} with pyrazolate derivatives (Murray *et al.*, 1988). The X-ray structure analysis of the title compound, bis(3,5-dimethylpyrazole- κN^2)silver(I) nitrate, was undertaken to investigate the possible coordination flexibility of the pyrazole ligands with Ag atoms. Coordination flexibility in silver(I) complexes ranges from two to eight. Depending on the reaction conditions and the particular pyrazolate ligand, the coordination will change, but linear structures are the most common. Among published silver–pyrazolate complexes, the average N—Ag—N angles and Ag—N distances are 169 (9)° and 2.167 (17) Å, respectively (Allen & Kennard, 1993).



The crystal structure of (I) reveals two independent silver–pyrazole units linked by nitrate ions. The resulting structure is almost centrosymmetric across the silver center. A potential center of symmetry at each Ag atom is broken by the deviation of the N—Ag—N moiety from linearity due to the


Figure 1

The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level for non-H atoms and H atoms are shown as spheres of arbitrary radii.

hydrogen bonds formed between the nitrate anion and the pyrazole ligand.

The Ag—N—N angles are 123.0 (2), 124.3 (3), 120.3 (2) and 120.8 (3)° (Table 1). A drawing of the title compound is shown in Fig. 1, and bond distances and angles are given in Table 1. Hydrogen-bonding distances are shown in Table 2. The angle formed by the planes of the two five-membered rings attached to each silver center is 12.1 (1)° for Ag1 and 9.7 (1)° for Ag2, and only a small deviation from linearity is observed in the coordination around silver. No π – π stacking is apparent in the crystal structure. The crystal packing showed that the silver–pyrazole units are linked by nitrates to form sheets, with Ag···N interactions between layers; the average Ag—N distance is 3.644 (4) Å. The hydrogen bonds formed between the NH groups and the nitrate anions are weak, with an average N···O distance of 3.01 (8) Å (Table 2). There is weaker hydrogen bonding to nitrate atoms N9 and N10 (see Table 2).

Experimental

The title compound was obtained by reaction of AgNO_3 with 3,5-dimethylpyrazole (1:2 stoichiometric ratio) in tetrahydrofuran (THF). Fine colorless crystals were obtained by slow evaporation of the solvent or by slow diffusion of hexanes into a THF solution of the title compound. The chosen crystals were coated with a hydrocarbon oil and mounted on a glass fiber.

Crystal data

 $[\text{Ag}(\text{C}_5\text{H}_7\text{N}_2)_2]\text{NO}_3$
 $M_r = 362.15$

 Triclinic, $P\bar{1}$
 $a = 10.030$ (1) Å

 $b = 11.336$ (1) Å

 $c = 13.656$ (2) Å

 $\alpha = 90.99$ (2)°

 $\beta = 109.47$ (2)°

 $\gamma = 101.01$ (3)°

 $V = 1431.4$ (3) Å³
 $Z = 4$
 $D_x = 1.680$ Mg m⁻³

 Mo $K\alpha$ radiation

Cell parameters from 4477 reflections

 $\theta = 2.5$ – 27.5 °

 $\mu = 1.42$ mm⁻¹
 $T = 213$ (2) K

Plate, colourless

 $0.46 \times 0.12 \times 0.09$ mm

Table 1
Selected geometric parameters (Å, °).

Ag1—N2	2.119 (3)	Ag2—N6	2.127 (3)
Ag1—N3	2.120 (3)	Ag2—N7	2.129 (3)
N2—Ag1—N3	175.51 (14)	N4—N3—Ag1	120.3 (2)
N6—Ag2—N7	174.44 (12)	N5—N6—Ag2	124.3 (3)
N1—N2—Ag1	123.0 (2)	N8—N7—Ag2	120.8 (3)

Data collection

Bruker SMART diffractometer ω scans	3871 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (<i>SADABS</i> ; Blessing, 1995)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.703$, $T_{\text{max}} = 0.884$	$\theta_{\text{max}} = 25.0^\circ$
7378 measured reflections	$h = -11 \rightarrow 11$
4913 independent reflections	$k = -12 \rightarrow 13$
	$l = -10 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 1.000P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.094$	$(\Delta/\sigma)_{\text{max}} = 0.022$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.14 \text{ e } \text{Å}^{-3}$
4913 reflections	$\Delta\rho_{\text{min}} = -1.02 \text{ e } \text{Å}^{-3}$
351 parameters	
H-atom parameters constrained	

H atoms were refined as riding, with N—H = 0.86 Å, C_{CH₃}—H = 0.96 Å and C_{CH}—H = 0.93 Å. The maximum and minimum residual electron-density peaks on the final difference Fourier map were located at distances of 0.86 and 0.96 Å from Ag2, respectively.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *SHELXL97*.

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>
N1—H1D···O2	0.86	2.20	2.945 (5)	145
N1—H1D···O3	0.86	2.23	3.029 (5)	155
N1—H1D···N9	0.86	2.56	3.417 (5)	171
N4—H4A···O6 ⁱ	0.86	2.14	2.956 (5)	159
N4—H4A···O4 ⁱ	0.86	2.34	3.083 (5)	144
N4—H4A···N10 ⁱ	0.86	2.59	3.446 (5)	171
N5—H5D···O3	0.86	2.08	2.930 (5)	170
N5—H5D···O1	0.86	2.41	3.069 (5)	134
N5—H5D···N9	0.86	2.60	3.430 (5)	162
N8—H8B···O5	0.86	2.15	2.937 (5)	153
N8—H8B···O6	0.86	2.35	3.133 (5)	151
N8—H8B···N10	0.86	2.62	3.477 (5)	177

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1637). Services for accessing these data are described at the back of the journal.

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