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Key indicators

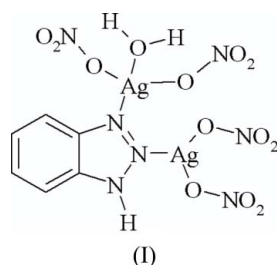
Single-crystal X-ray study
T = 294 K
Mean $\sigma(C-C)$ = 0.012 Å
R factor = 0.037
wR factor = 0.078
Data-to-parameter ratio = 12.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Poly[aqua- μ -1H-1,2,3-benzotriazole- μ -nitrate-nitratodisilver(I)]

A unique and stable silver benzotriazole complex, $[Ag_2(NO_3)_2(C_6H_3N_3)(H_2O)]_n$, is reported in which the benzotriazole is coordinated to the silver as a neutral donor ligand, bridging two silver atoms. Weakly bound nitrate anions and H_2O complete the coordination environment. The structure is built upon a chain of alternating units $[-Ag-HBZT-Ag-(NO_3)_2-H_2O-]$ where the three available bonding sites of the HBZT (1H-1,2,3-benzotriazole) ligand are fully occupied: two N atoms of the azine component are bound to silver and the third retains the original hydrogen.

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Comment

1H-1,2,3-Benzotriazole, HBZT, has been used as a stabilizer in conventional photographic systems for many years (James, 1977). Several metal complexes of benzotriazole have been reported, although not generally extensively investigated (Reedijk *et al.*, 1979, 1983; Meunier-Piret *et al.*, 1976). While silver benzotriazole, AgBZT, has been known since at least 1924 (Elbs *et al.*, 1924), its solid-state structure has only recently been reported (Rajeswaran *et al.*, 2006).



The inability to obtain crystals of AgBZT can be attributed at least in part to its poor solubility, $pK_{sp} = 13.4$ (Faerman, 1967); one advantage of the extremely low solubility is that benzotriazole can be used as an analytical reagent for silver (Cheng, 1954). During the course of our attempts to prepare AgBZT crystals suitable for X-ray crystal structure determination, its solubility in dilute nitric acid was considered a potential method (Elbs *et al.*, 1924). While crystals were obtained, they were found to have a structure corresponding to $Ag_2HBZT(NO_3)_2 \cdot H_2O$ (Fig. 1). This ligand is a neutral donor with the nitrate functioning as both ligand and counterion while the single water molecule provides a fourth ligand for one of the silvers. The Ag–N bond distances [2.248 (6) and 2.216 (7) Å] are within the normal range and compare well to values of 1.996 (15), 1.979 (9) and 2.202 (13) Å for the parent AgBZT (Rajeswaran *et al.*, 2006). The Ag–O bond distances are long, but not unusual for silver complexes (Jaber *et al.*, 1996), ranging from 2.365 (6) to 2.543 (6) Å.

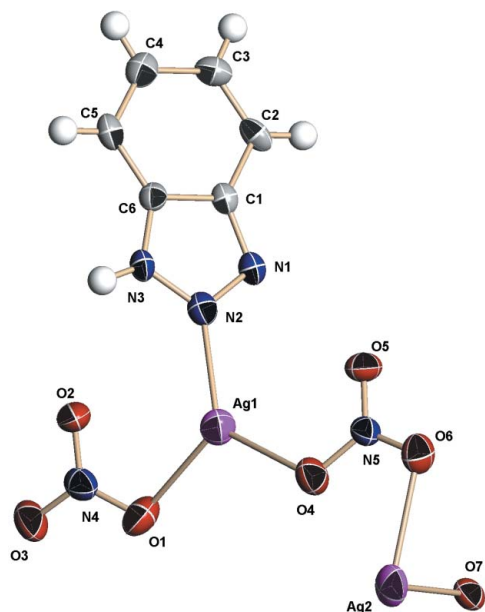


Figure 1
A diagram of part of the structure of $\text{Ag}_2\text{HBZT}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, showing 50% probability displacement ellipsoids and the atomic numbering scheme.

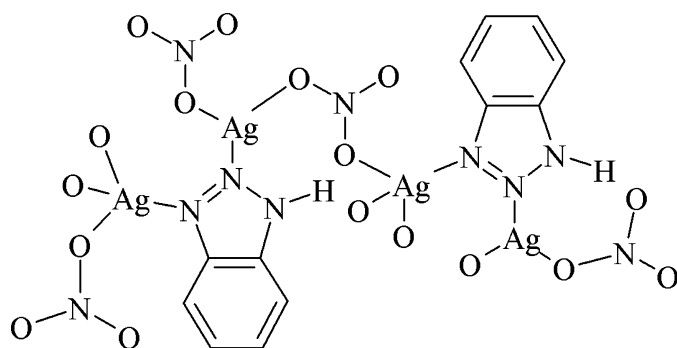


Figure 2
Schematic of the silver coordination environment in $\text{Ag}_2\text{HBZT}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$.

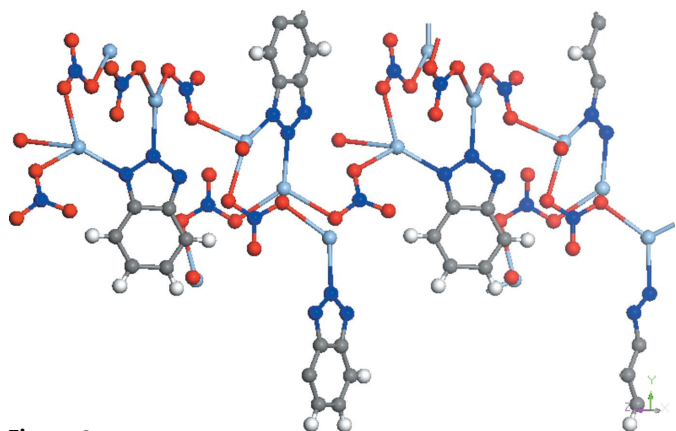


Figure 3
An illustration of the polymeric nature of the $\text{Ag}_2\text{HBZT}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ complex, showing interactions with the nitrate group.

One of the N atoms (N3) of the benzotriazole ring system is hydrogen bonded to the water O atom. A schematic diagram

of significant bonding interactions between the silver and the coordinating ligands is shown in Fig. 2. The three-dimensional packing pattern reveals a polymeric structure which requires participation of the nitrate groups (Fig. 3). The one other reported structure of a silver complex with benzotriazole as a ligand is $\text{Ag}(\text{HBZT})_2(\text{NO}_3)$ (Søtofte and Nielsen, 1983). In this case, the benzotriazole is also bound to the silver as a neutral donor, and the residual nitrate is a weakly coordinating counter-ion. Close inspection of the solid-state structures suggests that they could be considered intermediates in the formation of the nitrate-free AgBZT complex – that is $\text{Ag}_2\text{HBZT}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ rearranges to the $\text{Ag}(\text{HBZT})_2(\text{NO}_3)$ complex which then results in AgBZT *via* deprotonation of the ligand.

Experimental

AgBZT (1 g; Rajeswaran *et al.*, 2006) was added to 18.3 ml concentrated HNO_3 diluted in 155 ml H_2O . Heating to approximately 353 K provided a clear colorless solution. Slow cooling on standing produced fine rods that were collected and air dried. Attempts to prepare $\text{Ag}(\text{HBZT})_2(\text{NO}_3)$ by the reported procedure (Søtofte & Nielsen, 1983) were unsuccessful.

Crystal data

$[\text{Ag}_2(\text{NO}_3)_2(\text{C}_6\text{H}_3\text{N}_3)(\text{H}_2\text{O})]$
 $M_r = 474.89$
 Orthorhombic, $Pna2_1$
 $a = 7.0503(3) \text{ \AA}$
 $b = 10.9102(5) \text{ \AA}$
 $c = 15.0341(6) \text{ \AA}$
 $V = 1156.43(9) \text{ \AA}^3$

$Z = 4$
 $D_x = 2.728 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 3.43 \text{ mm}^{-1}$
 $T = 294(2) \text{ K}$
 Rod, white
 $0.20 \times 0.20 \times 0.02 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 $\varphi \omega$ scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.796$, $T_{\max} = 0.974$

8772 measured reflections
 2264 independent reflections
 1546 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.078$
 $S = 0.97$
 2264 reflections
 181 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.61 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.78 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 898 Friedel pairs
 Flack parameter: $-0.07(5)$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N3}-\text{H3} \cdots \text{O7}^i$	0.86	1.94	2.795 (8)	170

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

H atoms were positioned geometrically ($\text{N}-\text{H} = 0.86$, $\text{C}-\text{H} = 0.93 \text{ \AA}$) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997);

program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *MaterialsStudio* (Accelrys Inc., 2002); software used to prepare material for publication: *SHELXTL* and *MaterialsStudio*.

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