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Benzotriazole Complexes. IV. The Crystal Structure of Bis(benzotriazole)silver(I) Nitrate

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The crystal structure of the title compound, $[Ag(C_6H_5N_3)_2]NO_3$, has been investigated by X-ray diffraction techniques. The crystals are triclinic, space group $P\bar{1}$, with $a=10.048(2)$ Å, $b=10.311(3)$ Å, $c=14.817(1)$ Å, $\alpha=98.44(2)°$, $\beta=107.23(2)°$ and $\gamma=91.15(3)°$. The final R was 0.025. The structure consists of two crystallographically independent $Ag(C_6H_5N_3)_2^+$ ions and two independent NO_3^- ions. Each silver atom is coordinated to two nitrogen atoms, and the average Ag–N distances within the two ions are 2.149(3) Å and 2.196(10) Å. The corresponding N–Ag–N angles are 158.4(1) and 151.3(1)°. The coordination to silver has only a small effect on the geometry of the benzotriazole group. The packing of the structure may be described by layers of $Ag(C_6H_5N_3)_2^+$ ions separated by layers of NO_3^- ions. The shortest Ag–O distances are 2.630(3) Å and 2.679(3) Å. The distances to the next-nearest neighbours of Ag2 are Ag2–N2 of 2.469(3) Å and Ag2–O of 2.752(3) Å. The shortest Ag–Ag distance is 3.763(1) Å, found between Ag atoms related by a center of symmetry.

The present structure analysis is part of an investigation of benzotriazole complexes.[1–3] Benzotriazole is henceforth referred to as BTAH.

EXPERIMENTAL

Colourless crystals of $Ag(BTAH)_2NO_3$ were precipitated by mixing $4 \cdot 10^{-4}$ mol silver nitrate in 5 ml of 7 M ammonia with $3 \cdot 10^{-3}$ mol benzotriazole in 20 ml of 5 M nitric acid. Besides the title compound, triclinic crystals of another compound were precipitated, but since the crystals were of very poor quality, they have not been further investigated. Determination of the possible space groups and the data collection were carried out as described in Ref. 1. The dimensions of the crystal were 0.55×0.20×0.19 mm. The structure was solved by the Patterson technique.[4] The refinement technique and the references to atomic scattering factors are those given in Ref. 1. Crystal data and R-values are listed in Table 1. The final positional parameters with estimated standard deviations are listed in Table 2. The labelling of the atoms in the

Table 1. Crystal data.

M	408.1
μ(Mo$K\alpha$)(cm^{-1})	14.0
Crystal system	triclinic
V(Å^3)	1447.1
a (Å)	10.048(2)
b (Å)	10.311(3)
c (Å)	14.817(1)
α (°)	98.44(2)
β (°)	107.23(2)
γ (°)	91.15(3)
Space group	$P\bar{1}$
D_c (g cm^{-3})	1.87
Z	4
Total number of reflections	5068
Number of independent observations [$I \geq 2\sigma(I)$]	4271
$R=\sum\|\|F_o\|-\|F_c\|\|/\sum\|F_o\|$	0.025
$R_w=\left[\frac{\sum w(\|F_o\|-\|F_c\|)^2}{\sum w\|F_o\|^2}\right]^{\frac{1}{2}}$	0.033

0302-4377/83 $2.50

Table 2. Final atomic coordinates $\times 10^4$. The estimated standard deviations $\times 10^4$ are in parentheses. The values of the silver atoms and the values of the hydrogen atoms are multiplied by 10^5 and 10^3, respectively.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
N4	5930(3)	9419(3)	2785(2)	N5	424(3)	4276(3)	1636(2)
O1	4995(3)	9998(3)	2274(2)	O4	185(3)	3921(3)	754(2)
O2	6556(3)	8585(3)	2402(2)	O5	1278(3)	5199(3)	2074(2)
O3	6247(3)	9669(3)	3663(2)	O6	−149(3)	3651(3)	2085(2)
Ag1	13858(3)	47018(3)	38178(2)	Ag2	52566(3)	83930(2)	4671(2)
	BTAH 1				BTAH 2		
N1	−1429(4)	7626(3)	3829(3)		4274(3)	1853(3)	3725(2)
N2	−887(3)	6588(3)	3452(2)		3150(3)	2485(3)	3360(2)
N3	149(3)	6277(3)	4145(2)		3003(3)	3350(3)	4056(2)
C4	280(4)	7131(3)	4972(2)		4057(3)	3280(3)	4875(2)
C5	−749(4)	8007(3)	4766(2)		4891(4)	2299(3)	4666(2)
C6	−889(5)	9021(4)	5465(3)		6078(5)	2008(5)	5356(3)
C7	34(5)	9101(4)	6349(3)		6368(5)	2717(6)	6238(3)
C8	1074(6)	8211(5)	6563(3)		5526(5)	3707(5)	6461(3)
C9	1220(5)	7233(4)	5889(3)		4365(5)	4000(4)	5798(3)
H1	−199(5)	793(4)	347(3)		445(4)	130(4)	342(3)
H2	−156(4)	949(4)	531(3)		656(5)	145(5)	524(3)
H3	2(4)	968(4)	682(3)		713(5)	256(4)	668(3)
H4	173(5)	830(5)	718(4)		576(5)	415(4)	704(3)
H5	814(5)	325(4)	397(3)		383(4)	463(4)	591(3)
	BTAH 3				BTAH 4		
N1	2566(3)	5185(3)	497(2)		8307(3)	11377(2)	630(2)
N2	2905(3)	6368(3)	328(2)		7018(3)	10811(2)	353(2)
N3	4265(3)	6574(2)	669(2)		7100(3)	9586(2)	503(2)
C4	4816(3)	5516(3)	1073(2)		8487(3)	9365(3)	884(2)
C5	3714(3)	4613(3)	963(2)		9266(3)	10523(3)	968(2)
C6	3926(5)	3416(4)	1300(3)		10726(3)	10612(4)	1331(2)
C7	5286(5)	3181(4)	1745(3)		11335(3)	9493(4)	1573(3)
C8	6398(4)	4093(4)	1868(3)		10550(4)	8320(4)	1481(3)
C9	6191(4)	5267(3)	1539(2)		9127(4)	8226(3)	1146(3)
H1	175(5)	497(4)	35(3)		846(4)	1224(4)	58(3)
H2	328(4)	285(4)	121(3)		1121(4)	1131(3)	138(2)
H3	541(4)	242(4)	198(3)		1232(4)	957(4)	182(3)
H4	727(4)	392(4)	217(3)		1097(4)	761(4)	163(3)
H5	685(4)	583(3)	162(2)		859(4)	746(4)	105(3)

benzotriazole groups are as in Ref. 1. Lists of thermal parameters as well as lists of observed and calculated structure factors may be obtained from the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Bond lengths and bond angles with estimated standard deviations are listed in Table 3. The structure consists of two independent $Ag(BTAH)_2^+$ ions and two independent NO_3^- ions. Both silver atoms are coordinated to two N3 atoms. The Ag2–N3 bond lengths are somewhat larger than the Ag1–N3 bond lengths, but all four values fall within the range of values observed in other Ag-complexes.[5–13] The two N–Ag–N angles [158.4, 151.3°] are smaller than the corresponding angles [159–177°] found in the latter compounds.

The distances and angles for the Ag1 and Ag2 contact spheres are shown in Figs. 1 and 2,

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations. The figures in parentheses refer to numbers of the BTAH ligands.

Atoms	Distance or angle	Atoms	Distance or angle
Ag1–N3(1)	2.151(3)	Ag2–N3(3)	2.206(3)
Ag1–N3(2)	2.146(3)	Ag2–N3(4)	2.186(3)
N3(1)–Ag1–N3(2)	158.4(1)	N3(3)–Ag2–N3(4)	151.3(3)
N4–O1	1.243(4)	N5–O4	1.253(4)
N4–O2	1.244(4)	N5–O5	1.233(4)
N4–O3	1.229(4)	N5–O6	1.235(4)
O1–N4–O2	119.5(3)	O4–N5–O5	121.0(3)
O1–N4–O3	120.7(3)	O4–N5–O6	119.6(3)
O2–N4–O3	119.8(3)	O5–N5–O6	119.2(3)

Atoms	BTAH 1	BTAH 2	BTAH 3	BTAH 4
N1–N2	1.335(5)	1.328(4)	1.338(4)	1.330(4)
N2–N3	1.309(4)	1.306(4)	1.311(4)	1.314(4)
N3–C4	1.371(4)	1.366(4)	1.369(4)	1.378(4)
C4–C5	1.383(5)	1.384(5)	1.388(5)	1.384(4)
C5–N1	1.347(5)	1.352(4)	1.352(4)	1.353(4)
C5–C6	1.400(6)	1.393(5)	1.396(5)	1.401(4)
C6–C7	1.353(6)	1.346(7)	1.374(6)	1.362(6)
C7–C8	1.401(7)	1.403(8)	1.397(6)	1.397(6)
C8–C9	1.353(6)	1.357(6)	1.367(6)	1.364(5)
C9–C4	1.393(5)	1.400(5)	1.397(4)	1.399(5)
N1–H1	0.76(4)	0.74(4)	0.81(5)	0.92(4)
C6–H2	0.84(4)	0.80(5)	0.83(4)	0.85(4)
C7–H3	0.85(4)	0.88(4)	0.90(5)	0.95(4)
C8–H4	0.94(5)	0.87(5)	0.90(4)	0.87(4)
C9–H5	0.82(5)	0.88(4)	0.83(3)	0.92(4)
C5–N1–N2	112.0(3)	112.4(3)	111.2(3)	111.2(2)
N1–N2–N3	106.7(3)	107.0(3)	107.6(2)	108.2(2)
N2–N3–C4	109.7(3)	109.4(3)	109.2(3)	108.3(2)
N3–C4–C5	107.3(3)	107.9(3)	107.4(2)	107.8(3)
C4–C5–N1	104.3(3)	103.4(3)	104.5(3)	104.5(2)
C4–C5–C6	121.6(3)	121.6(3)	121.8(3)	121.5(3)
C5–C6–C7	116.7(4)	116.9(5)	116.2(4)	116.5(3)
C6–C7–C8	122.0(4)	122.1(4)	122.2(4)	122.0(3)
C7–C8–C9	121.7(4)	121.7(4)	121.6(4)	122.1(4)
C8–C9–C4	117.4(4)	116.8(4)	117.0(3)	116.5(4)
C9–C4–C5	120.7(3)	120.9(3)	121.1(3)	121.4(3)

respectively. In both $Ag(BTAH)_2^+$ ions the two benzotriazole molecules are almost parallel, the angle between the normals of the molecular planes being 5.6 and 10.0° for the Ag1- and Ag2-ions, respectively.

Besides the two nitrogen atoms, there are two nitrate oxygens within the contact sphere of Ag1. The Ag1–O5 and Ag1–O6 distances [2.630(3) and 2.679(3) Å] represent weak interactions between the atoms, and lie within the range of 2.5–2.8 Å found in other compounds.[5,7–15] The shortest Ag1–Ag1 distance is 5.062(1) Å, and is found to Ag1($\bar{x}$, $1-y$, $1-z$).

The contact sphere of Ag2 contains, apart from the N3 atoms from BTAH3 and BTAH4, one N2 atom and one nitrate oxygen. The Ag2–O2 distance [2.752(3) Å] is slightly larger than the largest Ag1–O distance. The N2 atom belongs to the BTAH4 group bonded to the silver atom related to Ag2 by the inversion center at ($\frac{1}{2}$, 1, 0). The Ag2–N2 distance of 2.493(4) Å indicates some interaction between the two atoms. Due to

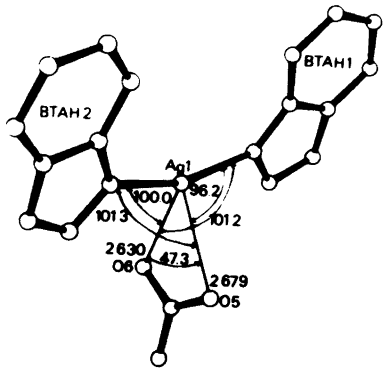

Fig. 1. The coordination around Ag1. The estimated standard deviations for the bond lengths and angles are 0.003 Å and 0.1°, respectively.[16] For Ag–N3 distanes and angles, see Table 3.

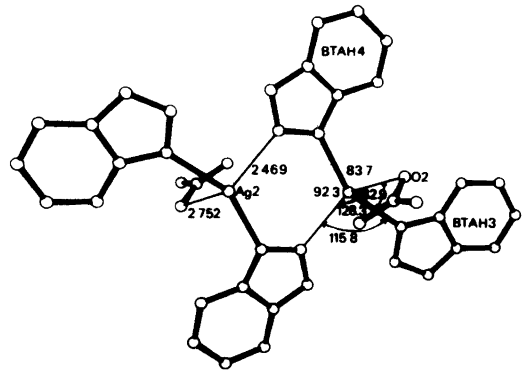

Fig. 2. The coordination around Ag2. The two Ag atoms are related by an inversion center. The estimated standard deviations for the bond lengths and angles are 0.003 Å and 0.1°, respectively. For Ag–N3 distances and angles, see Table 3.

the center of inversion the atoms N2 and N3 and their symmetry related atoms lie in a plane. The Ag2 atoms are 0.34 Å out of plane, and the Ag2–Ag2 separation [3.763(1) Å] is smaller than the separation of 4.251(2) Å found in bis[nitratobis(pentamethylenetetrazole)silver(I)][9] with a similar arrangement around the Ag atoms. In silver nitrate an Ag–Ag distance of 3.22 Å is found.[15]

The BTAH ligands are nearly planar, the deviation of the atoms from the least-squares planes through them being less than 0.02 Å. The sum of the endocyclic angles at C4 and C5 may be compared to idealized values (Ref. 3, Table 6). The idealized values are calculated as average values over triazole rings where the neighbouring atom to nitrogen is either H or C. For the $Ag1(BTAH)_2^+$ ion a comparison shows that the angles in the triazole groups correspond to intermediates between 1- and 1,3-substituted compounds. The triazole groups in the $Ag2(BTAH)_2^+$ ion corresponds more to 1-substituted compounds, which is in agreement with the longer Ag–N bonds found in this ion.

The nitrate ions are nearly planar, the deviations of the atoms from the least-squares planes through them being less than 0.02 Å. The symmetry of the nitrate ion is close to C_{2v} symmetry. Similar results are found in related compounds.

The packing of the structure is shown in Fig. 3. Layers of $Ag2(BTAH)_2^+$ ions ($z\sim0$) and layers of $Ag1(BTAH)_2^+$ ions ($z\sim\frac{1}{2}$) separated by nitrate ions repeat themselves in the direction of the

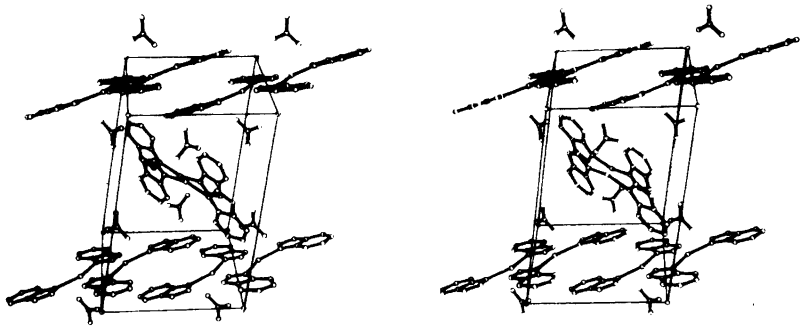

Fig. 3. Stereo view along the a^*-axis of the structure.

c-axis. This arrangement is also found in bis(imidazole)silver(I) nitrate.[7] The angles between the *ab*-plane and the BTAH planes are 76.0, 75.9, 84.4 and 86.6° for the BTAH1, BTAH2, BTAH3, and BTAH4 groups, respectively. For the N4 and N5 nitrate groups the corresponding angles are 89.5 and 80.7°, respectively.

The $Ag(BTAH)_2^+$ layers in the structure are linked *via* hydrogen bonds between nitrate oxygen atoms and N1 atoms. The N–H···O distances are N1(BTAH1)–O2($x-1, y, z$) [2.777(4) Å], N1(BTAH2)–O1($x, y-1, z$) [2.929(5) Å], N1(BTAH3)–O4(x, y, z) [2.851(4) Å], N1(BTAH3)–O5(x, y, z) [2.985(5) Å], and N1(BTAH4)–O6($1+x, 1+y, z$) [2.990(3) Å].

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