# The Crystal Structure of Ag₂BrNO₃

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$Ag_2BrNO_3$ is orthorhombic, space group *Pnma*, with $a = 6.8461$ (4), $b = 5.1320$ (4), $c = 12.8232$ (8) Å, $Z = 4$. The Br atoms are coordinated to five Ag atoms forming trigonal bipyramidal polyhedra which are linked by edges and corners, creating cavities in which the $NO_3$ groups are located.

## Introduction

Cationic complexes of the type $Ag_nX^{(n-1)+}$, with $X =$ Cl, Br or I, and $n \leq 4$, exist in aqueous-solution and molten-salt media (Holmberg, 1976 and references therein). The nature of the chemical bonding and the structural features of such complexes are, however, largely unknown. Several crystalline compounds of general formula $Ag_nX_xA_y$ ($n > x$) have been prepared with various anions $A$, but so far the crystal structure is known only for $Ag_3I(NO_3)_2$ (Birnstock & Britton, 1970). A brief report on $Ag_2BrNO_3$ and $Ag_2IF.H_2O$ has been given (Holmberg & Persson, 1975). The present paper is part of a systematic structural investigation of compounds of the above type with various $X$, $A$, $n$ and $x$, aiming at a clarification of the Ag coordination to the halide ion in the solid state.

## Experimental

Crystals of $Ag_2BrNO_3$ were obtained by saturation of a ~10 $M$ aqueous solution of $AgNO_3$ with AgBr at 90°C. After filtration at this temperature thin, colourless needles crystallized on cooling.

$Ag_2BrNO_3$ is stable in dry air at room temperature. The surface of the crystals darkens after exposure to light for a few days. This darkening had no significant effect on the intensities. The composition of the compound was checked by analyses for AgBr and total Ag. The density was determined by displacement in benzene.

Table 1 gives details of the crystal data, the collection of intensities, and the refinement. The method employed in data collection has been described (Elding, 1976). Weissenberg photographs revealed the Laue class *mmm* and the systematic absences $0kl: k + l = 2n$ + 1 and $hk0: h = 2n + 1$. A single-crystal diffractometer (CAD-4) was used for data collection. The cell dimensions were improved by least-squares refinement of 58 reflexions (Danielsson, Grenthe & Oskarsson, 1976). The wavelength was 0.70930 Å.

Three standard reflexions (217, 218, and 008), checked after every 50th measurement, showed random fluctuations <6%. The values of $I$ and $\sigma_c(I)$, where $\sigma_c(I)$ is the standard deviation based on counting

Table 1. *Crystal data, collection and reduction of intensities and the least-squares refinement*

| | | | |
|---|---|---|---|
| $Ag_2BrNO_3$, FW | 357.65 | $\mu$(Mo $K\alpha$) (cm⁻¹) | 172.6 |
| Crystal system | Orthorhombic | Range of transmission factor | 0.495–0.651 |
| Space group | *Pnma* | Number of measured reflexions | 1510 |
| $a$ (Å) | 6.8461 (4) | Number of reflexions given zero weight ($I < 0$) | 545 |
| $b$ (Å) | 5.1320 (4) | Number of independent reflexions used in the final | 965 |
| $c$ (Å) | 12.8232 (8) | refinement, $m$ | |
| $Z$ | 4 | Number of parameters refined, $n$ | 42 |
| $D_x$ (g cm⁻¹) | 5.27 | $R = \Sigma \|\|F_o\| - \|F_c\|\|/\Sigma \|F_o\|$ | 0.056 |
| $D_m$ (g cm⁻¹) | 5.2 | $R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$ | 0.037 |
| Crystal size (mm) | 0.045 × 0.187 × 0.028 | $S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$ | 1.38 |
| Radiation (graphite-monochromated) | Mo $K\alpha$ ($\lambda$ 0.71073 Å) | $a$ (weighting function) | 0.011 |
| Take-off angle (°) | 3 | $g \times 10^{-4}$ (extinction) | 0.46 (3) |
| $l\omega$ (°) ($\omega$–$2\theta$ scan) | 0.70 + 0.50 tan $\theta$ | Mosaic spread (″) | 12.5 |
| $l\theta$ (°) | 3–40 | Domain size (cm) | 0.33 × 10⁻⁴ |
| Minimum number of counts in a scan | 3000 | | |
| Maximum recording time (s) | 180 | | |

statistics, were corrected for Lorentz, polarization, and absorption effects. The expression $p = (\cos^2 2\theta_M + \cos^2 2\theta)/(1 + \cos^2 2\theta_M)$ with $\theta_M = 6\cdot08°$ was used in the correction for polarization. The crystal shape was described by eight planes.

## Structure determination and refinement

The structure was solved with a set of 481 independent intensities obtained photographically. The Ag and Br atoms were located by symbolic addition (Karle & Karle, 1963, 1966). A subsequent difference synthesis revealed the N and O atoms. At this point diffractometer data were recorded, and all further calculations were based on these. Full-matrix least-squares refinement, minimizing $\Sigma w(|F_o| - |F_c|)^2$, was performed with weights $w = 1/[\sigma_c^2/(4F_o^2) + (aF_o)^2]$. The applied constant $a$ gave too small weights on about 200 very weak reflexions ($\theta > 30°$), but apart from this it gave constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ in different $|F_o|$ and $\sin \theta$ intervals. The unusual result, $R_w < R$, is a consequence of the weighting function. Two scale factors, positional and anisotropic thermal parameters were refined (Table 1).

Scattering factors were from *International Tables for X-ray Crystallography* (1974). The final refinement also included correction for extinction (Zachariasen,
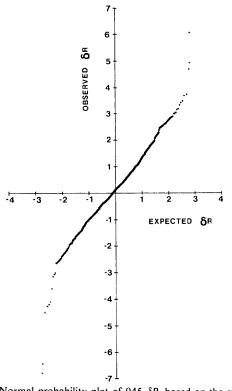


Fig. 1. Normal probability plot of 945 $\delta R_i$ based on the structure factors.

1967) and anomalous dispersion by Ag and Br. Only five reflexions had extinction corrections >10% in $|F_o|$.

In the last cycle the shifts in the parameters were <1% of the estimated standard deviations and the refinement was considered complete. A final difference synthesis showed a peak of height 2·5 e Å$^{-3}$ near Ag(1) but apart from this it was featureless.

Fig. 1 shows a normal probability plot of $\delta R(i) = [|F_o(i)| - |F_c(i)|]/\sigma|F_o(i)|$ against the values expected for a normal distribution (Abrahams & Keve, 1971). The plot is close to linear with a slope of 1·27 and an intercept of 0·13. The positive intercept indicates a systematic overestimation of $|F_o| - |F_c|$. This is partly because the method used in the measurements gives too small values for the background, and partly because of the large number of weak reflexions. The slope indicates that the values of $\sigma(F_o)$ are slightly underestimated.

All computations were made on the Univac 1108 computer in Lund. Final positional parameters are given in Table 2.*

## Description of the structure

Selected interatomic distances and angles are given in Table 3. Except for O(2) all atoms are located in the mirror planes at $y = \frac{1}{4}$ and $\frac{3}{4}$. Fig. 2 gives a stereoscopic picture of the content of the unit cell. The structure comprises a three-dimensional network of trigonal bipyramidal $Ag_5Br$ units sharing Ag(2) corners and Ag(1)—Ag(1) edges. The $NO_3$ group resides in a cavity formed by seven Ag atoms.

$Ag_2BrNO_3$ is the antitype of $BaCdS_2$ (Iglesias, Pachali & Steinfink, 1974) a structure topologically the same as $BaCdO_2$ (von Schnering, 1962). Fig. 3 gives a projection of $Ag_2BrNO_3$ along b. The N atom is located approximately at the Ba position in $BaCdS_2$.

Fig. 4 shows the $Ag_5Br$ unit. The trigonal bipyramid is distorted: the angle Ag(1$^{ii}$)—Br—Ag(2) is

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Table 2. *Positional parameters with estimated standard deviations*

|  | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ag(1) | 0·25039 (9) | $\frac{1}{4}$ | 0·03348 (5) |
| Ag(2) | 0·14514 (8) | $\frac{3}{4}$ | 0·25637 (5) |
| Br | 0·38291 (9) | $\frac{3}{4}$ | 0·08959 (5) |
| N | 0·35269 (79) | $\frac{1}{4}$ | 0·35078 (43) |
| O(1) | 0·21273 (74) | $\frac{1}{4}$ | 0·29141 (47) |
| O(2) | 0·42580 (52) | 0·45958 (90) | 0·38074 (28) |

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *with estimated standard deviations*

The superscripts (i) to (vii) are used to indicate the following equivalent sites in the structure:

| | | | |
|---|---|---|---|
| (i) | $\frac{1}{2}+x,$ $y,$ $\frac{1}{2}-z;$ | (ii) | $1-x,$ $1-y,$ $-z$ |
| (iii) | $x,$ $\frac{1}{2}-y,$ $z;$ | (iv) | $\frac{1}{2}-x,$ $\frac{1}{2}+y,$ $\frac{1}{2}+z$ |
| (v) | $-\frac{1}{2}+x,$ $y,$ $\frac{1}{2}-z;$ | (vi) | $x,$ $1+y,$ $z$ |
| (vii) | $x,$ $\frac{1}{2}-y,$ $z.$ | | |

| | | | |
|---|---|---|---|
| Ag(1)–Br | 2·817 (1) | Ag(2)–O(1$^{vi}$) | 2·646 (1) |
| Ag(1$^{vi}$)–Br | 2·817 (1) | Ag(2$^i$)–O(2) | 2·751 (4) |
| Ag(1$^{ii}$)·Br | 2·959 (1) | Ag(2$^i$)–O(2$^{vii}$) | 2·751 (4) |
| Ag(2$^i$)·Br | 2·665 (1) | Ag(2)–O(2) | 2·908 (4) |
| Ag(2)–Br | 2·692 (1) | Ag(2)–O(2$^{vii}$) | 2·908 (4) |
| Ag(1)·O(1) | 3·317 (6) | N·O(1) | 1·224 (8) |
| Ag(1$^i$)–O(2) | 2·703 (4) | N·O(2) | 1·247 (5) |
| Ag(1$^i$)–O(2$^{iii}$) | 2·703 (4) | N·O(2$^{iii}$) | 1·247 (5) |
| Ag(1$^{iv}$)–O(2) | 2·741 (4) | O(1)·O(2) | 2·144 (6) |
| Ag(1$^{iv}$)–O(2$^{vii}$) | 2·741 (4) | O(1)–O(2$^{iii}$) | 2·144 (6) |
| Ag(2)–O(1) | 2·646 (1) | O(2$^{iii}$)–O(2) | 2·151 (9) |

| | | | |
|---|---|---|---|
| Ag(1$^{ii}$)–Br–Ag(2) | 159·62 (3) | Ag(1$^{vi}$)–Br–Ag(2$^i$) | 114·02 (2) |
| Ag(1)–Br–Ag(2) | 90·34 (2) | Ag(1)–Br–Ag(1$^{vi}$) | 131·23 (3) |
| Ag(1)–Br–Ag(1$^{ii}$) | 97·95 (2) | Br–Ag(2)–Br$^v$ | 175·23 (3) |
| Ag(1$^{ii}$)·Br–Ag(2$^i$) | 80·07 (3) | O(1)–N–O(2) | 120·4 (3) |
| Ag(2)–Br–Ag(2$^i$) | 79·55 (2) | O(1)–N–O(2$^{iii}$) | 120·4 (3) |
| Ag(1)–Br–Ag(2$^i$) | 114·02 (2) | O(2)–N–O(2$^{iii}$) | 119·2 (6) |

159·62 (3)° and Br is 0·136 Å outside the equatorial plane. The shortest Ag–Br distances are found between Ag(2) and Br, which form a zigzag chain –Br–Ag(2)–Br–Ag(2)–Br– along **a**. The angles Br–Ag(2)–Br are 175·23 (3)°, and the Ag–Br distances in this quasi-linear unit are 2·665 (1) and 2·692 (1) Å, considerably shorter than those found in AgBr (2·887 Å) (Berry, 1955) but of the same magnitude as those found in compounds having Br in excess over Ag (Stomberg, 1969), where Ag is tetra-
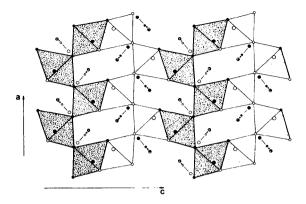
hedrally coordinated by Br. The strongest Ag–Br bonds in $Ag_2BrNO_3$ are found in this almost linear $AgBr_2$ segment, compatible with the pronounced



Fig. 3. A projection of the structure along **b**. Large circles Br, small Ag. Open circles are at $y = \frac{1}{4}$ and filled at $y = \frac{3}{4}$.
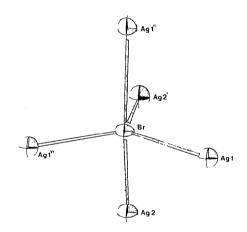


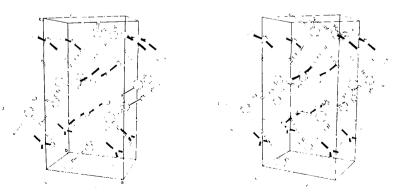Fig. 4. The trigonal bipyramidal silver coordination of bromine.



Fig. 2. A stereoscopic pair of drawings showing the content of the unit cell. Large circles Br, small Ag. Figs. 2, 4–6 have been drawn by *ORTEP2*.
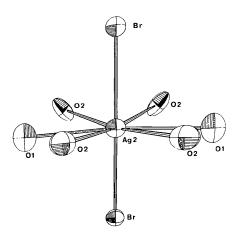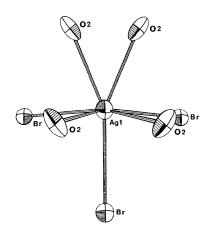
Fig. 5. The environment of Ag(2).



Fig. 6. The environment of Ag(1).

stability of two-coordinate Ag halide complexes in solution.

Ag(2) has six O atoms from four $NO_3$ groups as nearest neighbours, besides the two Br atoms of the zigzag chain. These O atoms constitute an almost planar six-membered ring around Ag (Fig. 5). The largest deviation of an O atom from the least-squares plane is 0·133 Å, and Ag(2) is 0·140 Å outside this plane. The Br—Ag(2)—Br axis is perpendicular to the O plane. The distances Ag(2)—O are quite long: 2·65–2·91 Å. A comparison may be made with the structure of orthorhombic $AgNO_3$, where the five shortest Ag—O distances out of a total of eight fall in the range 2·48–2·58 Å (Gibbons & Trotter, 1971).

Ag(1) has seven nearest neighbours, three Br and four O atoms from three $NO_3$ groups (Fig. 6). The Ag(1)—O distances are also rather long, 2·70 and 2·74 Å.

The three shortest Ag—Ag distances are 3·427 (1), 3·625 (1), and 3·908 (1) Å, the shortest being Ag($2^i$)—Ag(2).

The $NO_3^-$ ion resides in a cation box, made up of seven $Ag^+$ ions in a monocapped trigonal prismatic configuration (Fig. 7). The close to perfect $D_{3h}$ symmetry of the $NO_3$ group and the comparatively long Ag—O distances may be taken as an indication of rather weak interactions between the $Ag^+$ and $NO_3^-$ ions.
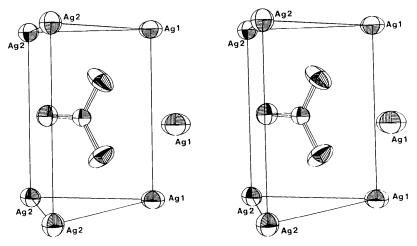
Fig. 7. A stereoscopic pair of drawings showing the $NO_3$ group in its cation box.

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# The Crystal and Molecular Structure of Tris(thiourea)copper(I) Hydrogen-o-phthalate. A Monomeric Trigonal Planar Copper(I) Complex

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$C_{11}H_{17}CuN_6O_4S_3$ is triclinic, space group $P\bar{1}$, with $a = 15\cdot342$ (9), $b = 15\cdot039$ (12), $c = 3\cdot946$ (4) Å, $\alpha = 89\cdot1$ (1), $\beta = 93\cdot6$ (1), $\gamma = 95\cdot6$ (1)°, $Z = 2$. The structure was refined to $R = 0\cdot059$ for 2725 counter reflexions. It consists of discrete trigonal planar $\{Cu[SC(NH_2)_2]_3\}^+$ ions held in slices parallel to (100) by NH···S hydrogen bonds and of hydrogen-o-phthalate anions linked to the cations through NH···O hydrogen bonds. Coordination to Cu is through S atoms [Cu–S = 2·247 (4), 2·230 (4), 2·238 (3) Å]. One of these is involved in an intramolecular hydrogen bond (N–H···S = 3·390 Å, N–H–S = 154°). The geometry of the hydrogen-o-phthalate anion corresponds to that expected, with the carboxylic groups twisted on opposite sides of the phenyl ring and forming a particularly short intramolecular hydrogen bond (O–H···O = 2·351 Å, O–H–O = 156°).

## Introduction

Cu$^I$ complexes with ligands containing S as donor atom, such as thiourea and its *N*-substituted derivatives, exhibit a wide variety of stoichiometries and configurations. Tetrahedral Cu$^I$ is found as discrete complexes in [Cu(tu)₄].½SiF₆ (tu = thiourea) (Hunt, Terry & Amma, 1974), [Cu(etu)₄]NO₃ (etu = ethylenethiourea) (Battaglia, Bonamartini Corradi, Nardelli & Vidoni Tani, 1976) and [Cu(dmtu)₃Cl] (dmtu = N,N'-dimethylthiourea) (Girling & Amma, 1971), as S-bridged dimers in [Cu₂(tu)₆](BF₄)₂, [Cu₂(dmtu)₆]-(BF₄)₂ (Taylor, Weininger & Amma, 1974) and [Cu₂(tu)₆](ClO₄)₂ (Hanic & Durcanska, 1969), and as polymeric chains sharing corners in [Cu(tu)₃]Cl (Okaya & Knobler, 1964). Tetrahedral Cu$^I$ alternating with S atoms form six-membered rings in [Cu₄(tu)₁₀]-

(SiF₆)₂.H₂O (Gash, Griffith, Spofford & Amma, 1973) and are arranged in polynuclear complexes in [Cu₄(tu)₉](NO₃)₄ (Vranka & Amma, 1966). Both tetrahedral and trigonal planar Cu$^I$ are found as binuclear complexes in [Cu₂(etu)₄Cl₂] (Battaglia, Bonamartini Corradi, Nardelli & Vidoni Tani, 1976) and as S-bridged chains in [Cu₂(tu)₅]SO₄.2H₂O (Belicchi Ferrari & Fava Gasparri, 1976). Finally, trigonal planar Cu$^I$ complexes are present as discrete ions in [Cu(etu)₃].½SO₄ and [Cu(tmtu)₃]BF₄ (tmtu = tetramethylthiourea) (Weininger, Hunt & Amma, 1972), and linked in chains sharing vertices in [Cu(tu)₂]Cl (Spofford & Amma, 1970). The only example of trigonal planar coordination in Cu$^I$ monomeric complexes involving unsubstituted thiourea is found in [Cu(tu)₃]Hpht (Hpht = hydrogen-o-phthalate), whose structure is reported in the present paper.