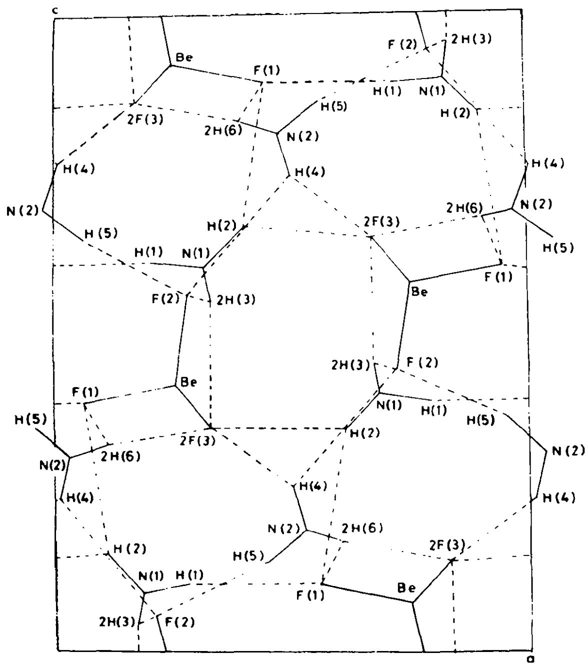

Fig. 1. An *xz* projection of a unit cell of $(NH_4)_2BeF_4$. Broken lines indicate hydrogen bonds.

distance of less than 2·9 Å, whereas all six F atoms around N(2) lie within 2·9 Å. If a sphere of radius 3·1 Å is considered, two more F atoms can be added around N(2) but none around N(1). The average N(2)—F distance then becomes 2·922 Å. In Table 4, H···F distances less than 2·6 Å and the corresponding N—H···F bond angles are given. The hydrogen-bonding scheme is depicted by broken lines in the *y* projection of the unit cell which is shown in Fig. 1. Each $NH_4^+$ tetrahedron is bonded to its neighbouring $BeF_4$ tetrahedra by eight hydrogen bonds. If H···F distances less than 2·01 Å are considered, then $(NH_4^+)_I$ is strongly hydrogen bonded to its neighbouring $BeF_4$ tetrahedra by one (2·01 Å) and $(NH_4^+)_{II}$ by three (2·01, 1·93, 1·93 Å) hydrogen bonds. The corresponding distances in $(NH_4)_2SO_4$ (Schlemper & Hamilton, 1966) are 1·97 Å and 1·85, 2·05, 2·05 Å respectively.

Schlemper & Hamilton (1966) have also determined the structure of $(NH_4)_2SO_4$ in the ferroelectric phase. They have attributed the transition to changes in hydrogen bonding. Jain, Bist & Upreti (1973) have, on the basis of spectroscopic evidence, ascribed the ferroelectric transition in $(NH_4)_2SO_4$ to a sudden distortion of sulphate ions at the transition temperature. An accurate crystal structure determination of $(NH_4)_2BeF_4$ in the low-temperature ferroelectric phase should help to reveal the transition mechanism in these crystals.

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# Structure of Disilver Chloride Nitrate

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**Abstract.** $Ag_2ClNO_3$, $M_r = 313{\cdot}19$, orthorhombic, *Pnma*, $a = 6{\cdot}6566\,(4)$, $b = 5{\cdot}1113\,(2)$, $c = 12{\cdot}4887\,(14)$ Å, $Z = 4$, $D_x = 4{\cdot}89$ Mg m$^{-3}$. The structure was refined anisotropically from single-crystal diffractometer data to an $R$ value of 0·028. The Cl 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. $Ag_2ClNO_3$ is isomorphous with $Ag_2BrNO_3$.

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**Introduction.** Compounds of the general formula $Ag_nX_xA_y$ ($n > x$), with $X$ = Cl, Br or I, are the subject of a systematic structural investigation aiming at a clarification of the Ag coordination to the halide in the solid state. The crystal structures of $Ag_3I(NO_3)_2$ (Birnstock & Britton, 1970), $Ag_2INO_3$ (Persson, 1979), $Ag_2BrNO_3$ (Persson & Holmberg, 1977), and $Ag_{13}I_9(WO_4)_2$ (Chan & Geller, 1977) are known. Brief reports on $Ag_2IF.H_2O$ (Holmberg & Persson, 1975) and $Ag_7I_2F_5.2H_2O$ (Persson, 1977) have been given.

Crystals of $Ag_2ClNO_3$ were prepared by saturation of an ~10 $M$ aqueous solution of $AgNO_3$ with AgCl at about 363 K. After filtration at this temperature thin, colourless needle-shaped single crystals were obtained on cooling.

The yield of $Ag_2ClNO_3$ obtained in this way was insufficient for direct chemical analysis and experimental density determination. The identity of the compound was therefore confirmed by comparison of the powder X-ray diffraction pattern with that from a powder obtained by rapid quenching of a 1:1 AgCl–$AgNO_3$ melt.

$Ag_2ClNO_3$ 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 serious effect on the X-ray intensities (see below). Table 1 gives information concerning the collection of intensities, and the refinement. The method employed in data collection has been described (Elding, 1976).

Weissenberg photographs showed the structure to be isomorphous with that of the analogous bromide compound, $Ag_2BrNO_3$, previously studied at this Institute. The intensity data were collected on a single-crystal diffractometer (CAD-4), and the cell dimensions were improved by least-squares refinement of 50 reflexions (Danielsson, Grenthe & Oskarsson, 1976). The wavelength used for the determination of the cell dimensions was 0·70930 Å (Mo $K\alpha_1$).

Table 1. *Details of the collection and reduction of intensity data, and the least-squares refinement*

| | |
|---|---|
| Crystal size (mm) | 0·063 × 0·406 × 0·050 |
| Radiation (Nb filter) | Mo $K\alpha$ ($\lambda = 0{\cdot}71073$ Å) |
| Take-off angle (°) | 3 |
| $\Delta\omega$ (°) ($\omega$–$2\theta$ scan) | 0·70 + 1·00 tan $\theta$ |
| $\Delta\theta$ (°) | 3–35 |
| Minimum number of counts in a scan | 3000 |
| Maximum recording time (s) | 180 |
| $\mu$(Mo $K\alpha$) (mm$^{-1}$) | 9·63 |
| Range of transmission factor | 0·580–0·648 |
| Number of measured reflexions | 1011 |
| Number of reflexions given zero weight | 406 |
| Number of independent reflexions used in the final refinement, $m$ | 605 |
| Number of parameters refined, $n$ | 42 |
| $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$ | 0·028 |
| $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$ | 0·032 |
| $S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$ | 1·55 |
| $a$ (weighting function) | 0·012 |
| $g \times 10^{-4}$ (extinction) | 0·53 (4) |
| Mosaic spread (seconds of arc) | 10·9 |
| Domain size (mm) | 0·38 × 10$^{-3}$ |

Three standard reflexions, checked every second hour, showed random fluctuations <5%. The values of $I$ and $\sigma_c(I)$, where $\sigma_c(I)$ is the standard deviation based on counting statistics, were corrected for Lorentz, polarization, and absorption effects. The crystal shape was described by eight planes.

Preliminary atomic coordinates for all atoms were taken from the $Ag_2BrNO_3$ structure. Full-matrix least-squares refinement, minimizing $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, was performed with weights $w = 1/[\sigma_c^2/(4F_o^2) + (aF_o)^2]$. The constant $a$ was chosen to make the average values $\langle w(\lvert F_o\rvert - \lvert F_c\rvert)^2\rangle$ almost equal in different $\lvert F_o\rvert$ and $\sin\theta$ intervals. Two scale factors, positional and anisotropic thermal parameters were refined (Table 1).

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final refinement also included correction for extinction (Zachariasen, 1967) and anomalous dispersion by Ag and Cl. Thirteen reflexions had extinction corrections >10% in $\lvert F_o\rvert$. In the last cycle the shifts in the parameters were less than 0·3% of the standard deviations and the refinement was considered complete. A final difference map showed a peak of height 1·8 e Å$^{-3}$ in the vicinity of Ag(1) but apart from this it was featureless.

Fig. 1 shows a normal probability plot of $\delta R(i) = \lvert\lvert F_o(i)\rvert - \lvert F_c(i)\rvert\rvert/\sigma\lvert F_o(i)\rvert$ *versus* the values expected for a normal distribution (Abrahams & Keve, 1971). The slope and intercept of the least-squares line fitted to all data are 1·38 and 0·08. The positive intercept may indicate a small overestimation of weak intensities (Persson & Holmberg, 1977). If this systematic error in $\lvert F_o\rvert$ is neglected, the value of the slope indicates that $\sigma(\lvert F_o\rvert)$ is underestimated by about 40%. It is still in acceptable agreement with the value of the e.s.d. of an observation of unit weight ($S$ = 1·55, Table 1). All

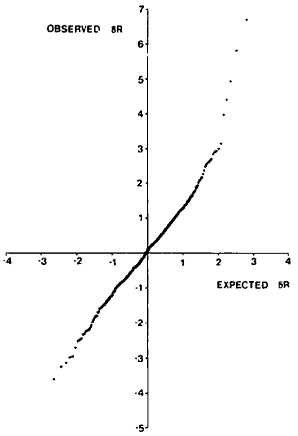

Fig. 1. Normal probability plot of 605 $\delta R_i$ based on the structure factors.

Table 2. *Positional parameters with estimated standard deviations*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ag(1) | 0·26723 (7) | $\frac{1}{4}$ | 0·03658 (5) |
| Ag(2) | 0·14538 (7) | $\frac{3}{4}$ | 0·25441 (4) |
| Cl | 0·38923 (20) | $\frac{3}{4}$ | 0·08872 (11) |
| N | 0·35484 (68) | $\frac{1}{4}$ | 0·35224 (33) |
| O(1) | 0·20774 (70) | $\frac{1}{4}$ | 0·29115 (45) |
| O(2) | 0·42868 (45) | 0·46010 (78) | 0·38194 (25) |

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

**Discussion.** A stereoview of the unit cell is given in Fig. 2. Selected interatomic distances and angles are listed in Table 3. O(2) is the only atom not located in the mirror planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The structure comprises a three-dimensional network of trigonal-bipyramidal $Ag_5Cl$ units sharing Ag(2) corners and Ag(1)—Ag(1) edges. The $NO_3$ group resides in a cavity formed by seven Ag atoms.

$Ag_2ClNO_3$ is, just like $Ag_2BrNO_3$, the antitype of $BaCdS_2$ (Iglesias, Pachali & Steinfink, 1974). For a detailed structure description of $Ag_2ClNO_3$ the reader is referred to the recent paper on $Ag_2BrNO_3$ (see above). Some aspects are, however, given here.

Three of the five Ag—Cl distances are of the same magnitude as those found in AgCl (2·777 Å; Nicklow & Young, 1963), whereas two are significantly shorter. These two are located in the almost linear $AgCl_2$ segment of the zigzag chain —Cl—Ag(2)—Cl—Ag(2)—Cl—. The angle Cl—Ag(2)—Cl of this $AgX_2$ segment is closer to 180° than in $Ag_2BrNO_3$ (Table 3). In compounds with more pronounced two-coordination between Ag and the halide, *e.g.* $Cs_2AuAgCl_6$ (Elliott & Pauling, 1938), the Ag—Cl distance is much shorter, 2·36 Å; this is approximately the sum of the ionic radii for $Ag^+$ and $Cl^-$ when both are two-coordinated.

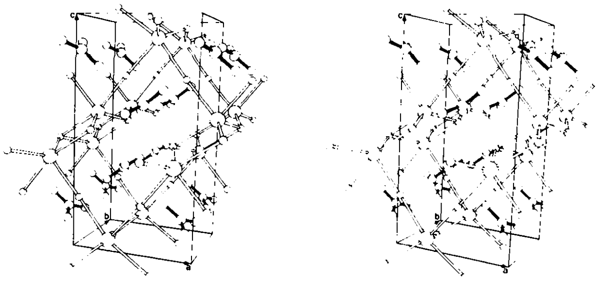

Fig. 2. A stereoscopic pair of drawings showing the contents of the unit cell. Large circles are Cl and small Ag. The figure has been drawn by the program *ORTEP* II (Johnson, 1971).

The Ag surroundings are described, with figures, in the $Ag_2BrNO_3$ paper. The nearest neighbours of Ag(2) describe an almost planar six-membered ring of O atoms, besides two Cl atoms which are situated one above and one below this plane. The deviations from the least-squares oxygen plane of the Ag(2) environment have approximately the same values for the chloride as for the bromide compound.

The three shortest Ag—Ag distances are 3·330 (1), 3·572 (1), and 3·820 (1) Å.

Within the accuracy of the measurements the $NO_3^-$ ion has perfect $D_{3h}$ symmetry. All O atoms are equidistant to the N atom and the angles O—N—O are 120° (Table 3).

The difference in silver-to-halide coordination geometry between $Ag_2ClNO_3$ and $Ag_2BrNO_3$ on the one hand and $Ag_2INO_3$ ($Ag_6I$ trigonal prisms) on the other may be due to variations between the halides in directional demands of partially covalent Ag—$X$ coordinate bonds, but it might also be attributed to simple packing effects, reflecting the variations in size of the halide ions. The ionic radii (CN = 6) differ between $Cl^-$ and $Br^-$ by 0·15 Å only, whereas the difference between $Br^-$ and $I^-$ amounts to about 0·24 Å (Shannon, 1976).

The help given by Dr Åke Oskarsson during the data collection is gratefully acknowledged. This work is part of a project supported by the Swedish Natural Science Research Council.

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) $x, \frac{3}{2} - y, z$.

| | | | |
|---|---|---|---|
| Ag(1)—Cl | 2·760 (1) | Ag(2)—O($1^{vi}$) | 2·629 (1) |
| Ag($1^{vi}$)—Cl | 2·760 (1) | Ag($2^{i}$)—O(2) | 2·679 (3) |
| Ag($1^{ii}$)—Cl | 2·771 (1) | Ag($2^{i}$)—O($2^{vii}$) | 2·679 (3) |
| Ag($2^{i}$)—Cl | 2·597 (1) | Ag(2)—O(2) | 2·879 (3) |
| Ag(2)—Cl | 2·630 (1) | Ag(2)—O($2^{vii}$) | 2·879 (3) |
| Ag($1^{i}$)—O(2) | 2·696 (3) | N—O(1) | 1·241 (7) |
| Ag($1^{i}$)—O($2^{iii}$) | 2·696 (3) | N—O(2) | 1·238 (4) |
| Ag($1^{iv}$)—O(2) | 2·761 (3) | N—O($2^{iii}$) | 1·238 (4) |
| Ag($1^{iv}$)—O($2^{vii}$) | 2·761 (3) | O(1)—O(2) | 2·145 (5) |
| Ag(2)—O(1) | 2·629 (1) | O(1)—O($2^{iii}$) | 2·145 (5) |
| | | O($2^{iii}$)—O(2) | 2·148 (8) |

| | | | |
|---|---|---|---|
| Ag($1^{ii}$)—Cl—Ag(2) | 162·49 (6) | Ag($1^{vi}$)—Cl—Ag($2^{i}$) | 111·79 (3) |
| Ag(1)—Cl—Ag(2) | 90·23 (3) | Ag(1)—Cl—Ag($1^{vi}$) | 135·68 (6) |
| Ag(1)—Cl—Ag($1^{ii}$) | 96·29 (3) | Cl—Ag(2)—Cl$^{v}$ | 177·08 (5) |
| Ag($1^{ii}$)—Cl—Ag($2^{i}$) | 83·35 (4) | O(1)—N—O(2) | 119·8 (2) |
| Ag(2)—Cl—Ag($2^{i}$) | 79·15 (4) | O(1)—N—O($2^{iii}$) | 119·8 (2) |
| Ag(1)—Cl—Ag($2^{i}$) | 111·79 (3) | O(2)—N—O($2^{iii}$) | 120·3 (5) |

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* Lists of structure factors, anisotropic thermal parameters and root-mean-square components of thermal displacement along the ellipsoid axes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34307 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Gold(III) Oxide

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**Abstract.** $Au_2O_3$, $M_r = 441{\cdot}93$, orthorhombic, $Fdd2$, $a = 12{\cdot}827\ (3)$, $b = 10{\cdot}520\ (3)$, $c = 3{\cdot}838\ (1)$ Å, $U = 517{\cdot}9$ Å$^3$, $Z = 8$, $D_x = 11{\cdot}33$, $D_m = 10{\cdot}6$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$) = 108·8 mm$^{-1}$. Empirical absorption corrections were applied to allow for suspected inhomogeneity of the crystal; the structure was refined to $R = 0{\cdot}058$ for 373 unique reflexions. The structure is polymeric; the Au atom shows square-planar coordination, and a *trans* effect is observed. Angles at O atoms are approximately tetrahedral. One O atom lies on a twofold axis and is coordinated to two Au [Au—O 1·93 (2) Å]; the other lies on a general position and is coordinated to three Au [Au—O 2·01 (2), 2·04 (2), 2·07 (2) Å].

**Introduction.** Gold has the least tendency of all metals to form simple compounds with oxide or hydroxide ligands. Although several oxoaurates have been characterized (Hoppe & Arend, 1962; Wasel-Nielen & Hoppe, 1968, 1970; Klassen & Hoppe, 1976), Au$^{\rm I}$ oxide and hydroxide are unknown, and $Au_2O_3$ was until recently unknown in anhydrous form. [The unidentified oxide $AuO_y$ reported by Muller, Newnham & Roy (1969) may be $Au_2O_3$ (Mohn, 1974).] We have previously reported the preparation of single crystals of $Au_2O_3$ (Schwarzmann, Mohn & Rumpel, 1976) and here report its crystal structure.

Intensities were measured with a Stoe four-circle diffractometer, monochromated Mo $K\alpha$ radiation and a crystal 0·2 × 0·2 × 0·1 mm. A complete sphere of data (1592 reflexions) was collected up to $2\theta = 60°$. Cell constants were obtained by least squares from strong high-angle reflexions. Lp corrections were applied, then empirical absorption corrections ($\mu = 108{\cdot}8$ mm$^{-1}$) based on measurements of strong equivalent reflexions at different azimuthal angles. Friedel opposites were also considered to be equal in deriving the absorption profile, since it was observed that reflexions with positive $l$ were systematically weaker than those with negative $l$. A possible explanation of the observed absorption is that a non-crystalline region was embedded asymmetrically in the crystal. This is consistent with the low observed intensities, high backgrounds and poor agreement of measured and calculated densities, and is also reasonable in view of the method of preparation of the crystals. Equivalent reflexions (not including Friedel opposites) were merged, rejecting all those for which measurements of all possible equivalent reflexions were not available (a few measurements were rejected because of high and asymmetric background

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