

temperature phase the static long-range ordered displacement wave (corresponding to the satellite reflections) takes the place of the thermal displacements in the high-temperature phase. The present results agree with the findings of inelastic neutron-scattering studies (de Pater & van Dijk, 1978; de Pater, Axe & Currat, 1978). In these measurements a rather strong quasi-elastic diffuse peak was observed at high temperature (423 K) which is centred in reciprocal space at a wave vector of $0.29\mathbf{c}^*$. This diffuse scattering is due to short-range correlated displacement fluctuations and an energy analysis yielded a relaxation time for the fluctuations of 2×10^{-11} s, at 423 K.

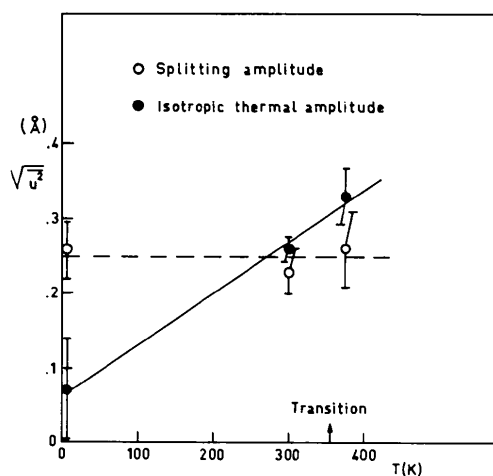


Fig. 3. Temperature dependence of the isotropic thermal amplitude: $(\bar{u}^2)^{1/2} \equiv (B/4\pi^2)^{1/2}$, where B is the overall Debye-Waller factor. The average splitting amplitude is also plotted, calculated from the data in Table 3.

In the present structure refinement these fluctuations in the normal high-temperature phase are seen as anisotropic smearing-out of the atoms.

In the low-temperature phase satellite reflections appear and the diffuse-scattering intensity decreases. The static displacements are seen as the splitting up of the atoms in the average structure. The splitting amplitude remains nearly constant in view of the decrease of the anisotropic thermal amplitude.

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References

- GIBBONS, C. S., REINSBOROUGH, V. C. & WHITLA, W. A. (1975). *Can. J. Chem.* **53**, 114–118.
- IZUMI, M., AXE, J. D., SHIRANE, G. & SHIMAOKA, K. (1977). *Phys. Rev. B*, **15**, 4392–4411.
- IZUMI, M. & GESI, K. (1977). *Solid State Commun.* **22**, 37–42.
- JAGER, G. DE (1978). Private communication.
- MOROSIN, B. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 744–745.
- PATER, C. J. DE (1978). *Phys. Status Solidi A*, **48**, 503–512.
- PATER, C. J. DE, AXE, J. D. & CURRAT, R. (1978) Unpublished.
- PATER, C. J. DE & VAN DIJK, C. (1978). *Phys. Rev. B*, **18**, 1281–1283.
- QUICKSALL, C. O. & SPIRO, T. G. (1966). *Inorg. Chem.* **5**, 2232–2233.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- STRIJKMANS, R. (1978). Private communication.

Acta Cryst. (1979). **B35**, 302–306

The Crystal Structure of Ag_2INO_3

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Abstract

Ag_2INO_3 is orthorhombic, space group $P2_12_12_1$ with $a = 7.4354(4)$, $b = 7.7759(4)$, $c = 17.1338(12)$ Å, and $Z = 8$. The structure was solved by direct methods from diffractometer data and was refined aniso-

tropically to an R value of 0.029. The I atoms are coordinated to six Ag atoms forming trigonal prisms which build up chains by sharing edges. The chains are linked together by either corners or edges. The NO_3 groups are located in the cavities of this three-dimensional network.

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Introduction

This work is part of a systematic structural investigation of compounds of the general formula $\text{Ag}_n\text{X}_x\text{A}_y$ ($n > x$) with various X , A , n and x . So far the detailed crystal structure is known for only three compounds meeting these stoichiometric requirements, *viz* $\text{Ag}_3\text{I}(\text{NO}_3)_2$ (Birnstock & Britton, 1970), Ag_2BrNO_3 (Persson & Holmberg, 1977), and $\text{Ag}_{13}\text{I}_9(\text{WO}_4)_2$ (Chan & Geller, 1977) which is an ionic Ag^+ conductor. Brief reports on $\text{Ag}_2\text{IF}\cdot\text{H}_2\text{O}$ (Holmberg & Persson, 1975), Ag_2INO_3 and $\text{Ag}_7\text{I}_2\text{F}_5\cdot 2\text{H}_2\text{O}$ (Persson, 1977) have been given.

Experimental

Crystals of Ag_2INO_3 were obtained by saturation of an $\sim 1.5 M$ aqueous solution of AgNO_3 with AgI at about 363 K. After filtration at this temperature colourless rods crystallized on cooling. The crystals appeared to be specimens of either Ag_2INO_3 or $\text{Ag}_3\text{I}(\text{NO}_3)_2$.

Ag_2INO_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. No chemical analyses could be carried out since the crystals obtained were a mixture of the two compounds Ag_2INO_3 and $\text{Ag}_3\text{I}(\text{NO}_3)_2$, and the total quantity of crystals was small. For the same reason the density was not determined experimentally.

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 Laue class *mmm* and the systematic absences $h00: h = 2n + 1$, $0k0: k = 2n + 1$ and $00l: l = 2n + 1$. A single-crystal diffractometer (CAD-4) was used for data collection. The cell dimensions were improved by least-squares refinement of 47 reflexions (Danielsson, Grenthe & Oskarsson, 1976). The wavelength was 0.70930 \AA .

The intensities of three standard reflexions (135, 248, and 2,5,11), checked after every 100 measurements, showed a small decrease and the intensities were scaled with the expression $Y = 1.0 - (0.56 \times 10^{-3}) X$, where X is the total time in hours that the crystal had been exposed to X-radiation. 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 expression $p = (\cos^2 2\theta_M + \cos^2 2\theta)/(1 + \cos^2 2\theta_M)$ with $\theta_M = 6.08^\circ$ was used in the correction for polarization. The crystal shape was described by ten planes.

Structure determination and refinement

The heavy-atom structure was solved using the *MULTAN* system of computer programs (Germain, Main & Woolfson, 1971). The O and N atoms were revealed in a subsequent difference synthesis. Full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, was performed with weights $w = 1/[\sigma_c^2/(4F_o^2) + (aF_o)^2]$. The value of a was chosen to give constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ in different $|F_o|$ and $\sin \theta$ intervals. One scale factor, and 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 I. Only nine reflexions had extinction corrections $> 10\%$ in $|F_o|$.

In the last cycle the shifts in the parameters were less than 0.5% of the estimated standard deviations and the refinement was considered complete. A final difference synthesis showed peaks of height $1.35 e \text{ \AA}^{-3}$ or less around the heavy atoms but it was otherwise featureless.

Fig. 1 shows a normal probability plot of $\delta R_{(i)} = [|F_o(i)| - |F_c(i)|] / \sigma |F_o(i)|$ versus the values expected for a normal distribution (Abrahams & Keve, 1971).

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

Ag_2INO_3 ; FW	404.65	μ (Mo $K\alpha$) (mm^{-1})	13.91
Crystal system	Orthorhombic	Range of transmission factor	0.364–0.565
Space group	$P2_12_12_1$	Number of measured reflexions	1673
a (\AA)	7.4354 (4)	Number of reflexions given zero weight ($I < 0$)	193
b (\AA)	7.7759 (4)	Number of independent reflexions used in the final refinement, m	1480
c (\AA)	17.1338 (12)	Number of parameters refined, n	128
Z	8	$R = \sum F_o - F_c / \sum F_o $	0.029
D_x (Mg m^{-3})	5.43	$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.030
Crystal size (mm)	$0.181 \times 0.056 \times 0.097$	$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	1.20
Radiation (graphite-monochromated)	Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$	a (weighting function)	0.015
Take-off angle ($^\circ$)	3	g ($\times 10^{-4}$) (extinction)	0.38 (2)
$\Delta\omega$ ($^\circ$) (ω - 2θ scan)	$0.50 + 1.30 \tan \theta$	Mosaic spread ($''$ of arc)	15.4
$\Delta\theta$ ($^\circ$)	3–30	Domain size (mm)	0.27×10^{-3}
Minimum number of counts in a scan	3000		
Maximum recording time (s)	180		

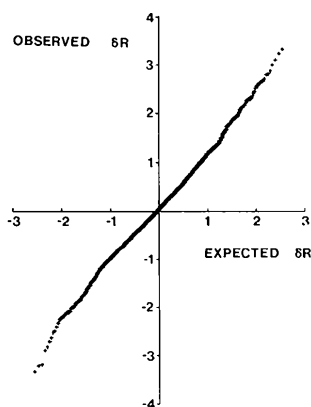


Fig. 1. Normal probability plot of 1474 δR_o based on the structure factors.

Table 2. Positional parameters with estimated standard deviations

	x	y	z
Ag(1)	0.67435 (11)	0.03154 (11)	0.44214 (4)
Ag(2)	0.24780 (11)	0.02963 (11)	0.44081 (4)
Ag(3)	0.71726 (11)	0.53074 (12)	0.31602 (5)
Ag(4)	0.32554 (11)	0.48515 (12)	0.30493 (4)
I(1)	0.47074 (8)	0.84270 (8)	0.32144 (3)
I(2)	0.45908 (8)	0.35323 (7)	0.44995 (3)
O(11)	0.46911 (96)	0.44874 (83)	0.76430 (31)
O(12)	0.62920 (94)	0.30936 (88)	0.68016 (42)
O(13)	0.33518 (98)	0.30268 (85)	0.67359 (36)
O(21)	0.45349 (99)	0.67090 (81)	0.61412 (34)
O(22)	0.63834 (100)	0.76749 (96)	0.52591 (38)
O(23)	0.41976 (103)	0.93288 (82)	0.56900 (34)
N(1)	0.47594 (94)	0.35369 (95)	0.70566 (36)
N(2)	0.50243 (96)	0.79035 (93)	0.57119 (37)

The plot is close to linear with a slope of 1.16 and an intercept of 0.08. The positive intercept indicates a systematic overestimation of $|F_o| - |F_c|$. This is because the method used in the measurements gives too small values for the background. 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. Fig. 2 gives a stereoscopic view of the contents of the unit cell. The structure consists of linked double

* 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 34032 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected interatomic distances (\AA) and angles ($^\circ$) with estimated standard deviations

Symmetry code		
(i)	$x, -1 + y, z$	(ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
(iii)	$-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$	(iv) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
(v)	$\frac{1}{2} + x, -1 + y, 1 - z$	(vi) $\frac{3}{2} - x, 1 - y, -\frac{1}{2} + z$
(vii)	$\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$	(viii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(ix)	$\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$	

Ag(1)—I(1 ⁱ)	2.954 (1)	Ag(3)—O(11 ^{vi})	2.500 (7)
Ag(1)—I(2 ⁱⁱ)	2.950 (1)	Ag(3)—O(12 ^{vi})	2.875 (7)
Ag(1)—I(2)	2.973 (1)	Ag(3)—O(13 ⁱⁱ)	2.743 (7)
Ag(2)—I(1 ⁱ)	3.007 (1)	Ag(3)—O(21 ^{ix})	3.147 (7)
Ag(2)—I(2)	2.971 (1)	Ag(3)—O(23 ^{ix})	2.496 (7)
Ag(2)—I(2 ⁱⁱⁱ)	2.990 (1)	Ag(4)—O(11 ^{viii})	2.356 (7)
Ag(3)—I(1)	3.042 (1)	Ag(4)—O(12 ⁱⁱⁱ)	2.728 (7)
Ag(3)—I(1 ^{iv})	3.105 (1)	Ag(4)—O(13 ^{viii})	3.036 (7)
Ag(3)—I(2)	3.295 (1)	Ag(1)—Ag(2)	3.172 (1)
Ag(4)—I(1 ^{iv})	2.865 (1)	Ag(3)—Ag(4)	2.940 (1)
Ag(4)—I(1)	2.996 (1)	I(1)—I(1 ^{iv})	4.615 (1)
Ag(4)—I(2)	2.866 (1)	I(1)—I(1 ^{viii})	4.615 (1)
Ag(1)—O(13 ⁱⁱ)	2.650 (7)	I(2)—I(1)	4.398 (1)
Ag(1)—O(21 ^{ix})	2.778 (7)	I(2)—I(1 ⁱ)	4.540 (1)
Ag(1)—O(22)	2.519 (7)	I(2)—I(1 ^{iv})	4.680 (1)
Ag(1)—O(23)	2.983 (7)	I(2)—I(2 ⁱⁱⁱ)	4.398 (1)
Ag(2)—O(12 ⁱⁱⁱ)	2.577 (7)	I(2)—I(2 ⁱⁱ)	4.398 (1)
Ag(2)—O(21 ⁱⁱⁱ)	2.847 (7)		
Ag(2)—O(22 ⁱⁱⁱ)	2.515 (7)		
Ag(2)—O(23 ⁱ)	2.651 (6)		
N(1)—O(11)	1.248 (9)	O(11)—O(12)	2.161 (9)
N(1)—O(12)	1.268 (10)	O(11)—O(13)	2.167 (9)
N(1)—O(13)	1.247 (10)	O(12)—O(13)	2.190 (10)
N(2)—O(21)	1.239 (9)	O(21)—O(22)	2.177 (10)
N(2)—O(22)	1.286 (10)	O(21)—O(23)	2.193 (9)
N(2)—O(23)	1.268 (10)	O(22)—O(23)	2.200 (10)
O(11)—N(1)—O(12)	118.35 (71)		
O(11)—N(1)—O(13)	120.59 (71)		
O(12)—N(1)—O(13)	121.06 (69)		
O(21)—N(2)—O(22)	119.01 (73)		
O(21)—N(2)—O(23)	122.03 (71)		
O(22)—N(2)—O(23)	118.93 (70)		
I(1 ⁱ)—Ag(1)—I(2 ⁱⁱ)	163.25 (4)		
I(1 ⁱ)—Ag(2)—I(2 ⁱⁱⁱ)	165.62 (4)		

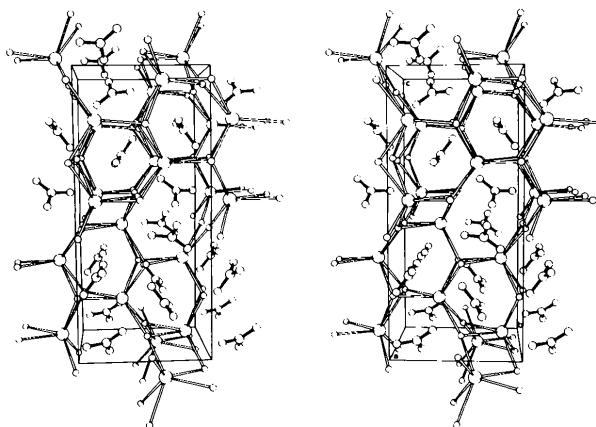


Fig. 2. A stereoscopic pair of drawings showing the contents of the unit cell. Large circles are I and small Ag. Figs. 2, 3, and 5–8 have been drawn by the program ORTEP II (Johnson, 1971).

chains, along **b**, containing trigonal-prismatic Ag_6I units. The prisms share Ag–Ag edges to form the double chains and these chains, two per unit cell, are linked by alternately shared Ag–Ag edges and Ag corners. The chains are of a zigzag type. The NO_3 groups reside in the cavities, formed by six Ag atoms, between the chains.

AgINO_3 is a new structure type but can be related to the structure of tungsten carbide, WC, through a twinning operation and a translation of $\frac{1}{2}a$. In the WC structure type, every second W trigonal prism is filled with C atoms. In the Ag_2INO_3 structure only every fourth of the Ag trigonal prisms is occupied. The twin plane is parallel with the *ab* plane through the trigonal prisms which lie on different levels and share edges (Fig. 3). The twin blocks are two filled trigonal prisms wide and the structure can be written symbolically as 4, 4, 4, 4 (Andersson & Hyde, 1974).

Fig. 4(a) and (b) shows the Ag_6I units of I(1) and I(2). The Ag–I(1) and Ag–I(2) distances range from 2.95–3.10 Å and 2.86–2.99 Å respectively, except for one, Ag(3)–I(2), which is 3.30 Å. The distances are longer than those found in $\beta\text{-AgI}$ (2.814 Å; Burley, 1963) but of the same magnitude as those observed in $\text{Ag}_3\text{I}(\text{NO}_3)_2$ (2.84–3.08 Å; Birnstock & Britton, 1970). In compounds $M_x\text{Ag}_n\text{I}_x$ with $x > n$ (Holmberg, 1976, references 26–39) the Ag–I distances fall in the approximate range 2.80–3.10 Å irrespective of the nature of the counterion *M*; therefore no significant difference in the Ag–I bonding strength can be inferred from such a comparison between bond lengths in the two general types of compounds.

The Ag surroundings are not easily described with a common polyhedron. Figs. 5–8 show the surroundings of the four different Ag atoms. Ag(1) has eight nearest neighbours: four O atoms, three I atoms, and one Ag atom. The O atoms and one of the I atoms make an irregular pentagon which approximately defines a plane. The five atomic positions deviate from the best-fitting least-squares plane by at most 0.07 Å and Ag(1) is located only 0.002 Å outside the plane. The other

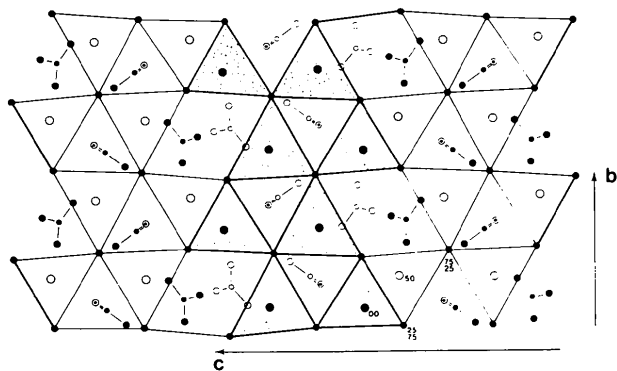


Fig. 3. A projection of the structure along **a**. Large circles are I and small Ag. The marked coordinates are idealized (see Table 2).

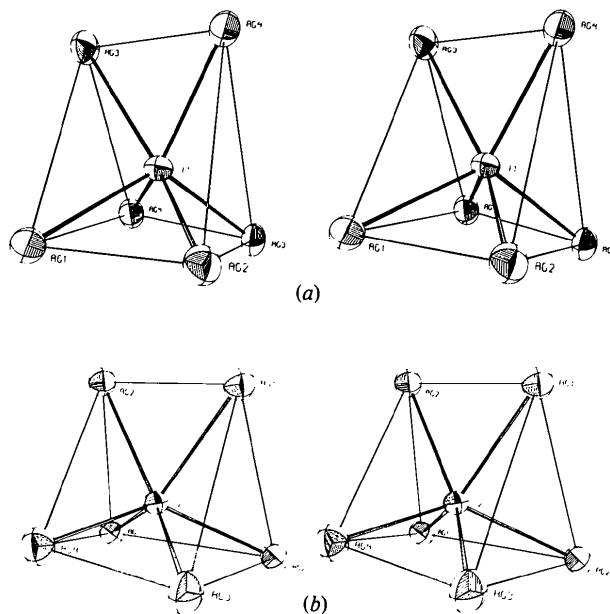


Fig. 4. Stereoscopic drawings showing the trigonal prisms around (a) I(1) and (b) I(2).

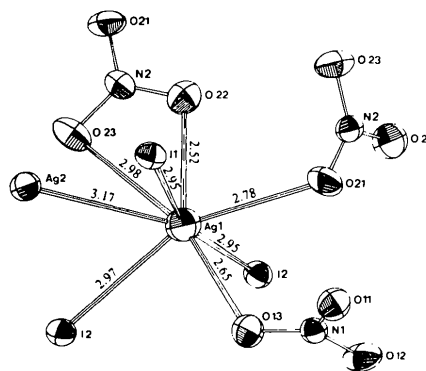


Fig. 5. The environment of Ag(1).

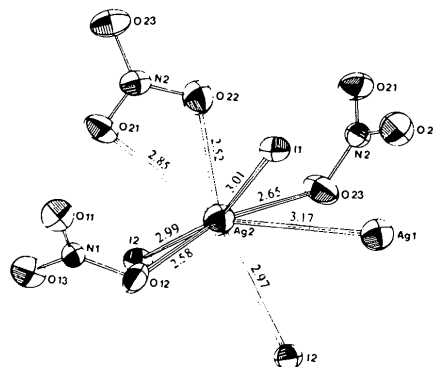


Fig. 6. The environment of Ag(2).

two I atoms are situated at each side of this pentagon; the plane defined by $\text{I}(1^i)$, $\text{I}(2^{ii})$, and $\text{Ag}(1)$ is close to perpendicular (89.7°) to the pentagon plane (*cf.* the Ag environment in Ag_2BrNO_3). The distances are given in the figures. All Ag—O distances in Ag_2INO_3 range from 2.36 to 3.04 Å (Table 3), and they are in good agreement with Ag—O distances found in $\text{Ag}_3\text{I}(\text{NO}_3)_2$.

$\text{Ag}(2)$ also has eight neighbouring atoms approximately in the same configuration as for $\text{Ag}(1)$. The pentagon is somewhat less ideal than in the $\text{Ag}(1)$ case. The deviations from the least-squares plane are at most 0.21 Å, $\text{Ag}(2)$ being 0.056 Å outside the plane. The $\text{I}(1^i)$, $\text{I}(2^{iii})$, and $\text{Ag}(2)$ plane makes an angle of 84.9° to the idealized plane of the five-membered ring. The position of the eighth atom, $\text{Ag}(1)$ [and $\text{Ag}(2)$ in the $\text{Ag}(1)$ environment], is clear from Figs. 5 and 6. The polyhedra of $\text{Ag}(1)$ and $\text{Ag}(2)$ share an $\text{O}(23)$ — $\text{I}(2)$ edge and an $\text{I}(1)$ corner.

The geometrical figure around $\text{Ag}(3)$ can be described as a distorted monocapped trigonal anti-

prism (Fig. 7). An $\text{Ag}(4)$ atom outside the I triangle makes the antiprism monocapped.

The $\text{Ag}(4)$ environment is given in Fig. 8, showing the seven nearest neighbours. The polyhedra of $\text{Ag}(3)$ and $\text{Ag}(4)$ share a face *via* the triangle of I atoms.

The NO_3 groups are located in the cavities between the chains of Ag_6I trigonal prisms. These cation boxes (*cf.* Ag_2BrNO_3) are formed by six Ag atoms and they also have the shape of a trigonal prism. The NO_3 group is oriented in this box with the O atoms directed towards the Ag—Ag edges. The NO_3 ions have close to perfect D_{3h} symmetry (Table 3).

Finally it should be observed that the Ag—X coordination in Ag_2XNO_3 is quite different for $X = \text{Br}$ and $X = \text{I}$. In the analogous bromide compound, Br is surrounded by five Ag atoms in a trigonal bipyramid. However, the structural similarities between Ag_2INO_3 and $\text{Ag}_3\text{I}(\text{NO}_3)_2$ are quite striking, both compounds being built up by chains of trigonal Ag_6I prisms.

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References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- ANDERSSON, S. & HYDE, B. G. (1974). *J. Solid State Chem.* **9**, 92–101.
- BIRNSTOCK, R. & BRITTON, D. (1970). *Z. Kristallogr.* **132**, 87–98.
- BURLEY, G. (1963). *J. Chem. Phys.* **38**, 2807–2812.
- CHAN, L. Y. Y. & GELLER, S. (1977). *J. Solid State Chem.* **21**, 331–347.
- DANIELSSON, S., GRENTHE, I. & OSKARSSON, Å. (1976). *J. Appl. Cryst.* **9**, 14–17.
- ELDING, I. (1976). *Acta Chem. Scand. Ser. A*, **30**, 649–656.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HOLMBERG, B. (1976). *Acta Chem. Scand. Ser. A*, **30**, 797–807.
- HOLMBERG, B. & PERSSON, K. (1975). *Acta Cryst.* **A31**, S65.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- PERSSON, K. (1977). Abstract PII. 79. 4th European Crystallographic Meeting, Oxford.
- PERSSON, K. & HOLMBERG, B. (1977). *Acta Cryst.* **B33**, 3768–3772.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

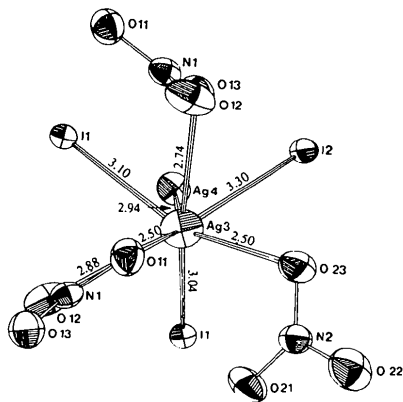


Fig. 7. The environment of $\text{Ag}(3)$.

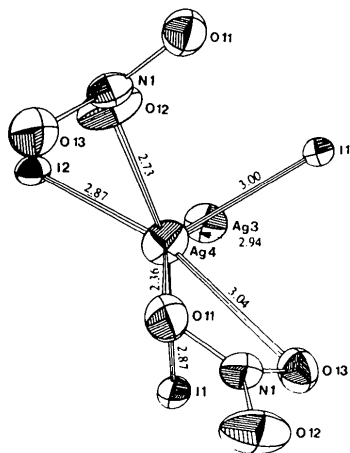


Fig. 8. The environment of $\text{Ag}(4)$.