

the Al—O and Si—O bonds are 1.746 (2) and 1.619 (2) Å respectively. In comparison with an ideal natrolite structure, 5% of the M^{1+} ($M = \text{Na, K}$) sites are occupied by M^{2+} ($M = \text{Ca, Mg}$) ions, therefore leaving another 5% vacant. Each Na(K) site is coordinated to six O atoms with an average distance of 2.45 Å forming a strongly distorted octahedron.

The application of the results of NMR measurements made it possible to determine, at least approximately, the positions of the H atoms, and from these data it follows that each water molecule participates in the formation of two hydrogen bonds [H(1)—O(1) 1.859 and H(2)—O(5) 1.878 Å] and two coordination bonds [Na—O(W) 2.412 and Na¹—O(W) 2.395 Å].

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Structure of Silver(I) Nitrite, a Redetermination

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Abstract. AgNO_2 , $M_r = 153.9$, orthorhombic, $Imm2$, $a = 3.528$ (1), $b = 6.172$ (1), $c = 5.181$ (1) Å, $V = 112.8$ (1) Å³, $Z = 2$, $D_x = 4.53$ Mg m⁻³, $\mu(\text{Ag } K\alpha) = 4.26$ mm⁻¹. The structure of AgNO_2 has been redetermined using a four-circle diffractometer with Ag $K\alpha$ radiation. The final R value is 0.024 for 1128 observed reflections. The Ag—N distance is 2.304 (2) Å, suggesting some covalency in the Ag—N bond. A large anisotropy in the atomic thermal vibrations was found.

Introduction. The crystal structure of AgNO_2 was first determined by Ketelaar (1936) from rotation and powder photographs and it was reinvestigated by Long & Marsh (1962) on the basis of Weissenberg photographs. Covalent radii of Ag and N atoms are 1.34 and 0.74 Å, respectively, the sum being 2.08 Å. The Ag—N distance derived by Ketelaar was 2.07 (30) Å, indicating complete covalency, whereas Long & Marsh reported it to be 2.47 (8) Å, which suggests a primarily ionic bond. It is probable that the Ag—N bond has appreciable covalency because AgNO_2 possesses the character of nitro compounds (for example, Makishima

& Tomotsu, 1954). The crystal structure has been reinvestigated in order to determine the Ag—N bond length more accurately.

Crystals of AgNO_2 were obtained by recrystallization from an acetonitrile solution of the commercial product in a dark room. Pale-yellow crystals grew as octahedra, exhibiting well developed forms of {110} and {011}. Weissenberg photographs confirmed the crystal geometry reported by Ketelaar (1936). Cell dimensions and intensity data were obtained with a spherical crystal 0.356 (16) mm in diameter on a Rigaku automated four-circle diffractometer at 300 K using Ag $K\alpha$ radiation ($\lambda = 0.5608$ Å) monochromated by a graphite plate. Cell dimensions were determined from 20 reflections ($40 < 2\theta < 46^\circ$), and agreed well with those reported by Long & Marsh (1962) (see Table 1). Intensities were collected for 2505 reflections in a hemisphere (the hkl , $h\bar{k}l$, $h\bar{k}\bar{l}$ and hkl sets; $2\theta \leq 100^\circ$), using a θ - 2θ continuous-scan technique at a speed of 2° min^{-1} in θ and with a scan width of $(1.3 + 0.5 \tan \theta)^\circ$. The room had been carefully kept dark in order to avoid exposing the specimen to light. During the period of data collection (8 days), intensities of the standard reflections did not decrease although the surface of the specimen turned black owing to the accumulation of metallic silver. A total of 1128 reflections with $|F_o| > 5\sigma(|F_o|)$ were

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Table 1. *Unit-cell dimensions*

Standard deviations are given in parentheses in this table and elsewhere in this paper.

	Ketelaar (1936)	Long & Marsh (1962)	This work
<i>a</i>	3.51 (1) Å	3.528 (2) Å	3.528 (1) Å
<i>b</i>	6.15 (1)	6.171 (1)	6.172 (1)
<i>c</i>	5.17 (2)	5.17 (2)	5.181 (1)

Table 2. *Determination of the absolute polarity*

<i>h k l</i>	$ F_o $	$ F_c $	$ F_o(h\bar{k}l) $	$ F_c(h\bar{k}l) $
3 $\bar{3}$ 2	11.66	11.71	0.99	0.98
3 $\bar{3}$ $\bar{2}$	11.76	11.90		
4 $\bar{3}$ 3	4.04	4.07	1.02	1.03
4 $\bar{3}$ $\bar{3}$	3.96	3.96		
3 $\bar{4}$ 3	8.84	8.40	1.07	1.02
3 $\bar{4}$ $\bar{3}$	8.23	8.27		
4 $\bar{2}$ 4	4.07	4.26	0.96	0.98
4 $\bar{2}$ $\bar{4}$	4.26	4.34		
3 $\bar{3}$ 4	9.81	10.01	0.96	0.98
3 $\bar{3}$ $\bar{4}$	10.20	10.18		
0 $\bar{3}$ 5	24.07	24.10	1.00	1.02
0 $\bar{3}$ $\bar{5}$	23.96	23.72		
2 $\bar{3}$ 5	13.93	13.85	1.03	1.02
2 $\bar{3}$ $\bar{5}$	13.59	13.60		
1 $\bar{8}$ 5	5.96	5.89	1.05	1.02
1 $\bar{8}$ $\bar{5}$	5.65	5.78		
4 0 6	2.20	2.23	0.96	0.98
4 0 $\bar{6}$	2.29	2.27		

used in the structure refinement, Bijvoet pairs being treated as independent.

Lorentz and polarization corrections were applied, as well as an absorption correction for a sphere with $\mu r = 0.76$ (Dwiggins, 1975). A three-dimensional Patterson synthesis was evaluated to find the Ag—N and Ag—O vectors. The estimated positional parameters z_N , y_O and z_O agreed with Long & Marsh's (1962) result, within their experimental errors. These coordinates were refined by the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) with isotropic thermal parameters to an *R* value ($= \sum |F_o| - |F_c| / \sum |F_o|$) of 0.33. The function minimized was $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where the weight w was defined by $w^{-1} = [\sigma_F(\text{counting})]^2 + (0.015|F_o|)^2$. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Introduction of anisotropic thermal parameters quickly reduced the *R* value to 0.04, suggesting large anisotropy of the temperature factors. The type II anisotropic secondary-extinction correction (Coppens & Hamilton, 1970) was applied. With the variation of azimuthal angle, ψ , the $|F_o|$ of 020 altered by 18%. The smallest extinction factor (F_o^2/F_c^2) was 0.62 for $\bar{1}\bar{1}0$. The final $R = 0.024$ and $R_w = 0.034$ for 1128

observed reflections.* The observed and calculated intensity ratios of the nine $h\bar{k}l$ and $h\bar{k}\bar{l}$ pairs, for which $|F_o(h\bar{k}l)|$ and $|F_c(h\bar{k}l)|$ differed by more than 1.5%, are compared in Table 2. The concordance in this table indicates that the absolute polarity is correct. The opposite structure with respect to the sense of polar direction was refined independently ($R_w = 0.035$) and it was rejected at the 0.005 significance level according to Hamilton's (1965) test. Neither the positional parameters nor the thermal parameters changed significantly when the wrong polarity was assumed, suggesting no significant polar-dispersion effect in the present case (Cruickshank & McDonald, 1967).

Discussion. Positional and thermal parameters obtained by the present study are compared with those reported previously in Table 3. The *z* coordinate of the N atom given by Long & Marsh (1962) differs markedly. This may be correlated with the underestimate of the thermal parameters of the N atom. Thermal parameters B_{ij} in Long & Marsh's paper are related to U_{ij} in the present work as $B_{ij} = 8\pi^2 U_{ij}$ (Cruickshank, 1956). They could account for the anisotropy of the temperature factors to some extent, but not precisely, owing to the limited precision of film data and the neglect of an absorption correction in spite of a large linear absorption coefficient, $\mu(\text{Cu } K\alpha) = 70.5 \text{ mm}^{-1}$. The interatomic distances and bond angle

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36143 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of atomic parameters*

	Ketelaar (1936)	Long & Marsh (1962)	This work
2Ag at (000); ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)			
2N at (00z); ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$)			
4O at (0yz); (0yz); ($\frac{1}{2}, \frac{1}{2} + y, \frac{1}{2} + z$); ($\frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$)			
z_N	0.40 (5)	0.478 (16)	0.4446 (4)
y_O	0.17 (1)	0.168 (9)	0.1701 (4)
z_O	0.50 (3)	0.576 (14)	0.5747 (4)
Ag U_{11}		0.056 (3)	0.0758 (2)
U_{22}		0.023 (3)	0.0374 (1)
U_{33}		0.034 (3)	0.0171 (1)
B_{eq}^*		3.0 (1)	3.43 (1)
N U_{11}		0.010 (10)	0.0459 (10)
U_{22}		0.014 (18)	0.0358 (9)
U_{33}		0.014 (22)	0.0172 (4)
B_{eq}		1.0 (8)	2.60 (4)
O U_{11}		0.057 (20)	0.0705 (11)
U_{22}		0.057 (20)	0.0362 (7)
U_{33}		0.033 (34)	0.0271 (6)
U_{23}		0.009 (15)	-0.0041 (5)
B_{eq}		3.9 (12)	3.52 (4)

* The equivalent isotropic thermal parameters, B_{eq} , have been calculated from $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

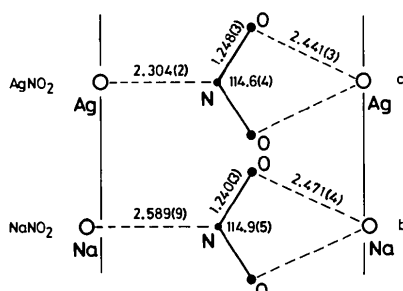


Fig. 1. Bond distances (Å) and bond angle ($^{\circ}$) for AgNO_2 and NaNO_2 (Kay & Frazer, 1961).

are shown in Fig. 1. The shortest Ag–N distance is 2.304 (2) Å, intermediate between 2.07 (30) Å (Ketelaar, 1936) and 2.47 (8) Å (Long & Marsh, 1962), suggesting some covalency in the Ag–N bond. The distances and bond angle for the nitrite ion agree very well with the neutron diffraction result of NaNO_2 (Kay & Frazer, 1961). The crystal structure of AgNO_2 is quite close to that of NaNO_2 (for example, see Table 1 of Gesi, 1970), which is ferroelectric below the transition point, *ca* 433 K (Sawada, Nomura, Fujii & Yoshida, 1958). On the other hand, the transformation to a non-polar state is not observed in AgNO_2 up to the decomposition temperature of about 413 K and polarization reversal by applied electric fields has not been reported (Gesi, 1970). The different character of the two nitrite crystals may be accounted for by the covalent Ag–N bond. Each Ag atom in AgNO_2 is surrounded by the N atom at 2.304 (2) Å, by two O atoms at 2.441 (3) Å and by four other O atoms at 2.722 (2) Å (see Fig. 2 of Long & Marsh, 1962). Each Na atom in NaNO_2 is surrounded by the N atom at 2.589 (9) Å, by two O atoms at 2.471 (4) Å and by four other O atoms at 2.499 (4) Å.

An attempt to observe the charge distribution around the NO_2^- ion, so that it could be compared with that of the coordinated nitrite ion in crystals of $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ (Ohba, Toriumi, Sato & Saito, 1978), was unsuccessful because of the unexpected large anisotropic thermal vibrations. In Table 4 the maximum and minimum root-mean-square deviations of the atoms in crystals of AgNO_2 , NaNO_2 (Kay & Frazer, 1961) and $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ are listed. A large anisotropy in thermal vibrations is found in AgNO_2 , the ratios of the largest and smallest mean dis-

Table 4. Root-mean-square displacements (Å)

u_{\max} and u_{\min} are the maximum and minimum vibrational displacements.

Crystal		u_{\max}	u_{\min}
AgNO_2	Ag	0.28 (1)	0.13 (1)
	N	0.21 (3)	0.13 (2)
	O	0.27 (3)	0.16 (3)
$\text{NaNO}_2^{(a)}$	Na	0.13 (2)	0.12 (2)
	N	0.13 (1)	0.11 (1)
	O	0.16 (1)	0.11 (1)
$\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]^{(b)}$	Co	0.10 (1)	0.10 (1)
	N	0.12 (1)	0.11 (1)
	O	0.18 (2)	0.11 (2)

(a) Kay & Frazer (1961). (b) Ohba, Toriumi, Sato & Saito (1978).

placements for Ag, N and O atoms being 2.1 (2), 1.6 (3) and 1.6 (3), respectively.

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