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A Reinvestigation of the Crystal Structure of Silver Nitrite*

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The crystal structure of silver nitrite, $AgNO_2$, which was originally determined by Ketelaar (1936), has been reinvestigated by X-ray diffraction methods. The only significant difference between our results and those of Ketelaar is the value for the Ag–N distance, which we find to be 2·47 ± 0·08 Å rather than 2·07 ± 0·3 Å. The longer distance indicates the interaction between the silver and nitrogen atoms to be primarily ionic rather than covalent in character.

The crystal structure of silver nitrite, $AgNO_2$, was first investigated by Ketelaar (1936). He found the crystals to be orthorhombic with space group *Imm*2, selecting this space group rather than *Immm* because of the expected symmetry of the NO_2 group and an observed hemimorphism of the crystals. In the structure derived by Ketelaar from rotation and powder photographs, the nitrite group lies on a two-fold axis which is parallel to *c* and which also contains the silver atom; since the *c* axis is only 5·2 Å in length (Table 1), the Ag–N distance must be rather short—2·6 Å at most. Indeed, the approximate *z* parameters selected by Ketelaar lead to a Ag–N distance of only 2·07 Å, suggesting some covalent character to the bond. In order to check on this surprising feature, we have undertaken a reinvestigation of the structure. Our results have confirmed the general structure derived by Ketelaar, but our *z* parameters lead to a more reasonable value of 2·47 ± 0·08 Å for the Ag–N distance.

Experimental

Reagent grade $AgNO_2$ was dissolved in warm water and allowed to cool slowly. Crystals formed in the shape of long, flat needles parallel to *c* and with principal faces (100). Because of their thinness the crystals tended to bend, but after some difficulty a satisfactory one was found; its dimensions were approximately 0·5 × 0·1 × 3·0 mm. This crystal was used for all our measurements.

The lengths of the *a* and *b* axes were determined from a rotation photograph about *c* in a Straumanis-type camera. The length of the *c* axis was determined only approximately and found to agree with Ketelaar's value. The unit-cell dimensions and estimated standard deviations are given in Table 1. The density calculated on the basis of two molecules of $AgNO_2$ in the unit cell is 4·54 g.cm.$^{-3}$; the value observed by Ray (1908) is 4·45 g.cm.$^{-3}$.

Table 1. *Unit-cell dimensions*

($\lambda_{\text{Cu } K\alpha} = 1 \cdot 5418$ Å)

	Ketelaar*	This investigation
a	3·51 ± 0·007	3·528 ± 0·002
b	6·15 ± 0·01	6·171 ± 0·001
c	5·17 ± 0·02	—

* Corrected to Ångstrøm units.

Intensities were visually estimated from Weissenberg photographs prepared with Cu *Kα* radiation for layer lines 0–5 about the *c* axis. The photographs gave clear indication of anisotropic absorption effects, which is not surprising in view of the shape of the crystal; the magnitude of the effect was such as to give rise to a difference of about 30% in intensity for some pairs of equivalent reflections. We did not make corrections to the measured intensities, but tried to take the effect into qualitative account by averaging equivalent readings. We recognize such a procedure to be inadequate, but although the resulting intensity estimates do not allow such factors as anisotropic temperature parameters or anomalous dispersion to be treated with accuracy we are confident they are adequate for the determination of atomic coordinates.

The photographs confirmed the body-centered lattice with the heavy silver atoms at the origin and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Furthermore, an electron density projection onto the centrosymmetric (001) zone calculated with all signs positive showed, besides peaks at (0, 0) and $(\frac{1}{2}, \frac{1}{2})$, only four other peaks at (0, 0·18); (0, 0·82); $(\frac{1}{2}$, 0·32); and $(\frac{1}{2}$, 0·68). These are consistent with the expected positions for the oxygen atoms of two nitrite groups centered at (0, 0) and $(\frac{1}{2}, \frac{1}{2})$, again in agreement with the structure proposed by Ketelaar. It remained only to check on the position of the nitrite groups along the *c* axis.

Structure factors for all observed reflections were then calculated including only the silver atoms. Wilson plots for the six different layer lines gave approximate values for the temperature factor and the six independent scale factors and also indicated that the temperature factor should be larger along *a* than along *b*. The resulting parameters together with the positional parameters of Ketelaar were the starting values for a series of least-squares refinements.

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Approximately twenty structure-factor least-squares cycles were calculated on a Burrough's 220 computer. During the first cycles the four positional parameters (z_{Ag}, z_{N}, z_{O}, y_{O}) and the anisotropic temperature parameters of the silver atom were optimized; anisotropic temperature factors for the nitrogen and oxygen atoms were included in the later refinements. The weighting function was chosen somewhat arbitrarily as $w=n^{\frac{1}{2}}F_o^{-4}$, where n, the total number of separate measurements of a given reflection, ranged from 1 to 12. The fourth-power dependence on F_o was chosen to represent our estimate of the square of the uncertainties in F_o^2, as $\Sigma w(F_o^2-F_c^2)^2$ was the quantity being minimized. Since all observed reflections are of at least medium intensity no tailing function to decrease the weight of weak reflections was used. The (110) reflection, which apparently suffers from extinction, was given an additional weighting factor of zero.

Three additional points might be mentioned. First, although there are formally three z parameters to be adjusted only two of them are independent, as c is a polar axis. Since our least-squares program does not compute off-diagonal terms between different atoms, we obtained sensible (but theoretically incorrect) shifts for all three z coordinates; these and all other parameters shifts we multiplied by $\frac{1}{2}$ and also translated the origin back to the silver atom before proceeding to the next cycle. Secondly, we were probably unjustified in including the anisotropic temperature factors of the light atoms as parameters in the least-squares calculations. Nevertheless, the output values (see Table 2) are not unreasonable except, perhaps, for the B_{11} term of the nitrogen atom. The only cross term permitted by the symmetries of the point positions, the B_{23} term for the oxygen atom, has the expected positive sign which implies greater thermal motion perpendicular to the N–O bond than parallel to it. Since the scaling between layer lines was empirical, the coefficient B_{33} is without significance. Third, the effect of anomalous dispersion for the silver atom was neglected. The real part of the correction term is small (Dauben & Templeton, 1955); the imaginary part, although larger in magnitude, is ineffective because of the small size of the B terms of the structure factors compared to the A terms (Table 3) and also because our observed intensities were averaged over two or more asymmetric units of reciprocal space.

Table 2. *The final parameters and their standard deviations*

2 Ag at $(0, 0, z;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z)$ (z_{Ag} was arbitrarily set at 0)
2 N at $(0, 0, z;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z)$
4 O at $(0, y, z);\ (0, \bar{y}, z);\ (\frac{1}{2}, \frac{1}{2}+y, \frac{1}{2}+z);\ (\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z)$

	Ketelaar	This investigation
z_{N}	$0{\cdot}4\ \pm0{\cdot}05$	$0{\cdot}478\pm0{\cdot}016$
y_{O}	$0{\cdot}167\pm0{\cdot}01$	$0{\cdot}168\pm0{\cdot}009$
z_{O}	$0{\cdot}50\ \pm0{\cdot}03$	$0{\cdot}576\pm0{\cdot}014$

Temperature factors

	B_{11}	B_{22}	B_{33}	B_{23}
Ag	$4{\cdot}4\pm0{\cdot}2$	$1{\cdot}8\pm0{\cdot}2$	$2{\cdot}7\pm0{\cdot}2$	—
N	$0{\cdot}8\pm0{\cdot}8$	$1{\cdot}1\pm1{\cdot}4$	$1{\cdot}1\pm1{\cdot}7$	—
O	$4{\cdot}5\pm1{\cdot}6$	$4{\cdot}5\pm1{\cdot}6$	$2{\cdot}6\pm2{\cdot}7$	$0{\cdot}7\pm1{\cdot}2$

The final parameters and their estimated standard deviations are given in Table 2. The observed and calculated structure factors are given in Table 3. The final R factor is 0·081.

At the conclusion of the refinement the section at $x=0$ of a three-dimensional difference map was calculated. In order to obtain an objective view of the nitrite group, only the contribution of the silver atom was included in F_c, and since the silver atom was placed at the origin its phase angle is always 0°. The differences F_o-F_c, then, were real and accordingly the map contains a center of symmetry not present in

Table 3. *Observed and culcalated structure factors*

Within each group the numbers, reading from left to right, are k, $10F_o$, $10|F_c|$, $10A_c$, and $10B_c$

The 110 reflection indicated by an asterisk (*) was given zero weight in the least-squares calculations

0k0					
	0	---	1401	1401	0
	2	672	742	742	0
	4	590	520	520	0
	6	397	388	388	0
1k0					
	1	645*	928	928	0
	3	455	484	484	0
	5	412	427	427	0
	7	238	254	254	0
2k0					
	0	542	650	650	0
	2	469	422	422	0
	4	344	324	324	0
	6	252	252	252	0
3k0					
	1	330	301	301	0
	3	214	200	200	0
	5	182	181	181	0
4k0					
	0	147	157	157	0
	2	102	119	119	0
0k1					
	1	541	585	584	-41
	3	605	660	656	75
	5	382	329	329	-11
	7	202	204	204	0
1k1					
	0	383	418	409	-87
	2	527	603	601	52
	4	418	419	419	20
	6	243	220	220	-10
2k1					
	1	386	327	327	-15
	3	431	368	367	37
	5	216	201	201	-5
3k1					
	0	192	156	155	-16
	2	232	198	198	15
	4	163	150	150	8
4k1					
	1	88	69	69	0
	3	84	77	77	10
0k2					
	0	---	905	893	145
	2	562	631	625	-89
	4	470	448	447	-38
	6	312	322	321	17
1k2					
	1	547	684	682	41
	3	504	455	446	-90
	5	369	352	352	12
	7	211	220	220	-1
2k2					
	0	468	490	487	60
	2	419	375	372	-44
	4	305	284	284	-23
	6	222	212	212	9
3k2					
	1	274	249	249	6
	3	202	188	185	-31
	5	154	153	153	1
4k2					
	0	127	130	129	6
	2	100	108	108	-13
0k3					
	1	418	445	443	-38
	3	389	397	384	98
	5	271	264	264	-9
	7	134	157	157	2
1k3					
	0	404	402	392	-89
	2	391	376	370	65
	4	286	291	289	36
	6	198	182	182	-13
2k3					
	1	294	263	262	-15
	3	261	238	231	57
	5	191	162	162	-3
3k3					
	0	166	142	141	-20
	2	170	137	134	26
	4	115	109	108	18
4k3					
	1	46	56	56	3
0k4					
	0	---	395	390	57
	2	396	400	397	-52
	4	292	296	294	-36
	6	175	194	194	7
1k4					
	1	361	354	354	13
	3	320	326	320	-62
	5	215	212	212	-1
2k4					
	0	242	251	249	26
	2	279	255	253	-34
	4	207	195	193	-26
3k4					
	1	147	151	151	-2
	3	122	142	139	-29
0k5					
	1	274	256	256	1
	3	193	181	176	42
	5	153	159	159	9
1k5					
	0	253	250	250	-12
	2	208	184	182	29
	4	142	153	151	27
2k5					
	1	177	158	157	5
	3	119	113	109	30

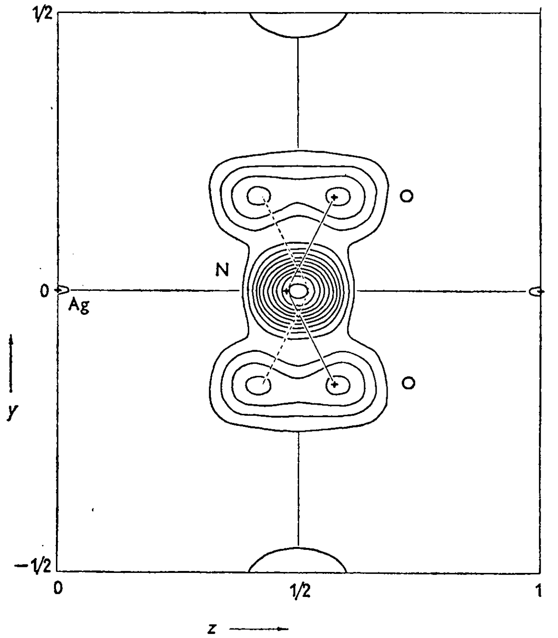

Fig. 1. The difference electron density in the section $x=0$. The calculated contributions of the silver atom were subtracted from the F_o values; the resulting values are real and accordingly the map has a false center of symmetry. The NO_2^- group is indicated by solid lines, its ghost by dashed lines.

the space group. As a result, two NO_2^- groups each of half weight appear superimposed on one another, one being real and the other its centrosymmetric ghost. This section is shown in Fig. 1.

Discussion of the results

A drawing of the structure is shown in Fig. 2. The dimensions of the nitrite ion in $AgNO_2$, together with those obtained by Kay & Frazer (1961) in a recent neutron diffraction investigation of the low-temperature form of $NaNO_2$, are given in Table 4. The agreement is satisfactory in view of the rather large uncertainties in this investigation.

The structure we have derived differs from that proposed by Ketelaar (1936) only in the location of the NO_2^- group on the c axis, and the difference is only slightly greater than the uncertainties in Ketelaar's z parameters. The structural implications, however, are quite different. We find the closest Ag–N distance to be 2·47 ± 0·08 Å rather than 2·07 ± 0·3 Å; and although this distance is short enough to suggest a definite interaction between the two atoms it is far too long for a covalent bond in the usual sense. That the interaction is primarily ionic in character is indicated by the calculations of Kay & Frazer (1961), who show that the observed spontaneous polarization of $NaNO_2$ (which is isostructural with $AgNO_2$, although the lengths of the b and c axes are considerably different) leads to a significant negative charge on the nitrogen atom.

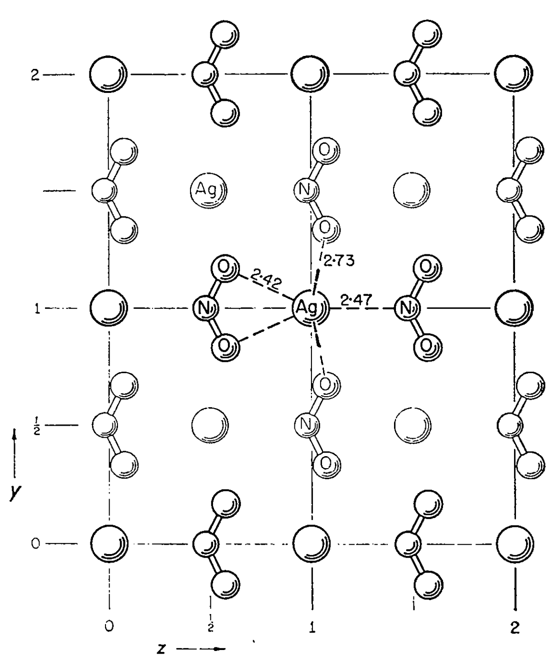

Fig. 2. The structure of $AgNO_2$ viewed along the a axis.

Table 4. *Interatomic distances, bond angles, and standard deviations for the nitrite ion in* $AgNO_2$ *and* $NaNO_2$

	$AgNO_2$	$NaNO_2$* (Kay & Frazer)
N–O	1·15 ± 0·07 Å	1·240 ± 0·003 Å
O–O	2·07 ± 0·11	2·090 ± 0·006
O–N–O	128 ± 15°	114·9 ± 0·5°

* The neutron diffraction results of Kay & Frazer are in close agreement with earlier X-ray diffraction results of Carpenter (1952, 1955) and of Truter (1954), but the estimated standard deviations are considerably lower.

Each silver ion is surrounded by the nitrogen atom at 2·47 ± 0·08 Å, by two oxygen atoms at 2·42 ± 0·07 Å and by four other oxygen atoms at 2·73 ± 0·04 Å. The Ag–O distances compare well with the values ranging from 2·4 to 2·6 Å found in $AgClO_2$ (Cooper & Marsh, 1961).

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