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The Crystal Structure of the Silver Perchlorate–Dioxane Complex, $AgClO_4.3C_4H_8O_2$*

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The structure of the crystalline complex formed by silver perchlorate with three molecules of dioxane has been determined. The crystals are cubic (a_0 = 7·67 Å) with Laue symmetry *m*3*m* and probable space group *Pm*3*m*; there is one molecule of the complex in the unit cell. The silver atoms, at the corners of the cube, are surrounded by a regular octahedron of dioxane oxygen atoms at a distance of 2·46 Å. Both the perchlorate ion, whose center is at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and the dioxane molecules, which lie along the axes of the unit cube, appear to be rotating with little or no hindrance.

Comyns & Lucas (1954) have recently characterized a crystalline complex of silver perchlorate with three molecules of dioxane. An investigation of the structure of this complex was deemed worthwhile because of both the general complex-forming ability of silver ion and the especially remarkable complexing properties of silver perchlorate (Sidgwick, 1950).

Experimental part

The complex was prepared according to the procedure of Comyns & Lucas (1954). Anhydrous silver perchlorate (2·2 g.) (Smith & Ring, 1937), dioxane (15 ml.) and acetone (15 ml.) were gently warmed until the solid dissolved. Well formed crystals were then obtained by slow evaporation at room temperature; the crystals were washed with acetone, after which the excess acetone was removed by a slow current of dry air. Microanalysis of a portion of the product indicated that it was the same as the substance isolated by Comyns & Lucas (Table 1). The analytical results correspond very well with those calculated for the complex of silver perchlorate with three dioxane, particularly in view of the fact that the crystals cannot be dried effectively (they lose dioxane readily at 120° C.), that they are quite hygroscopic, and that the silver in them is easily reduced even in the absence of direct sunlight.

Table 1. *Microanalyses of* $AgClO_4.3$ *dioxane*

	Calculated for $AgClO_4.3C_4H_8O_2$ (%)	Found, this work (%)	Found, Comyns & Lucas (%)
Ag	22·87	22·88	23·0*, 23·1*
Cl	7·52	7·42	7·60
C	30·56	31·05	29·9
H	5·13	5·34	5·13

All analyses except those followed by (*) were by Dr A. Elek.

* Analysis by A. E. Comyns.

Examination of the crystals with a polarizing microscope showed them to be isotropic. Suitable crystals were mounted for X-ray analysis by wedging them in special lithium-glass capillaries with a wall thickness of 0·01 mm. and an inside diameter of 0·2 mm. The crystals were found to be cubic, with Laue symmetry *m*3*m*. Long-exposure rotation and powder photographs showed that the unit cell was primitive, with a_0 = 7·67±0·01 Å. No accurate density measurement could be made because the crystals absorbed solvent readily and in so doing seemed to become more dense. The approximate density by flotation was 1·88 g.cm.$^{-3}$, which corresponds to one (calculated 1·08) molecule per unit cell.

Equi-inclination Weissenberg intensity photographs were taken with Cu $K\alpha$ radiation and the multiple-film technique for $h = 0$ through $h = 4$. Relative intensities were estimated visually with the aid of an intensity strip. The films were correlated by comparison of the appropriately corrected intensities of those reflections which appeared on more than one layer. A total of 137 independent reflections lie within the copper sphere of reflection for this crystal; of these, 132 were experimentally accessible under the conditions used and all were actually observed.

The crystals used for intensity photographs were approximately spherical with a diameter of 0·20 mm. Since the absorption coefficient of this compound for Cu $K\alpha$ radiation is 116·2 (*Internationale Tabellen*, 1935), the absorption of these crystals varied by a factor of nearly 2 as the diffraction angle θ changed from 0° to 90°. However, the nearly ideal shape of the crystals simplified the correction for absorption effects, and an approximate correction was applied just before the final structure-factor calculation.

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All calculations, except as otherwise indicated, were made with the high-speed computer SWAC by procedures described elsewhere (Sparks, Prosen, Kruse & Trueblood, 1956).

Determination and refinement of the structure

Since there is only one molecule of the complex in the unit cell, only space groups with onefold positions need be considered. Three space groups, *P*432, *P*$\bar{4}$3*m*, and *Pm*3*m*, satisfy this criterion and conform to the observed Laue symmetry, *m*3*m*. In each of these space groups there are two independent onefold positions, at the origin and at the center of the unit cell. Consequently, the silver and chlorine atoms must occupy these positions; the silver atom may be placed arbitrarily at the origin and the chlorine at the center. The perchlorate group, thus centered at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, is required to have the symmetry 43, $\bar{4}$3*m*, or *m*3*m* respectively in the three possible space groups; this requirement would of course be identical if the positions of the silver and chlorine atoms were interchanged. The tetrahedral perchlorate group could have apparent symmetry 43 or *m*3*m* only if disorder exists in the crystal.

The dioxane molecule as a whole must be in one of two threefold positions. These threefold positions occur in the same places in the three space groups, at the midpoints of the cell edges and at the centers of the cell faces. The point symmetry requirements for these positions are 42 for *P*432, $\bar{4}$2*m* for *P*$\bar{4}$3*m*, and 4/*mmm* for *Pm*3*m*. Neither the chair form, the boat form, nor any other reasonable configuration of the dioxane molecule possesses any of these point symmetries. A certain amount of randomness must therefore be assumed.

In order to determine in which of the two possible positions the dioxane molecule lies, an electron-density projection on (001) was calculated with phases (signs) based only upon the positions of the silver and chlorine atoms. All of the signs were determined by the silver position. Well resolved peaks were found at the origin and center of the unit cell, corresponding to the silver and chlorine atoms respectively, and also along the axes at ±0·32. The latter peaks were attributed to the oxygens of the dioxane molecules and indicated that the dioxane molecules lie along the cell edges. Thus the Ag–dioxane–Ag distance determines the unit-cell size. If one assumes a normal non-bonded Ag–O distance of 2·5 Å and an intramolecular O–O distance in dioxane of 2·8 Å (calculated from normal bond distances and angles), the predicted cell constant is 7·8 Å, which agrees well with the observed value, 7·67 Å.

Cigar-shaped peaks with an extension of about 2·3 Å intersected the axes at ±0·43. These peaks were presumed to correspond to the carbon atoms, either rotating, or arrayed in a disordered way in several discrete positions, some of which were real and some introduced by the center of symmetry assumed at the phasing stage. No peaks corresponding to the perchlorate oxygens were evident around the chlorine atom.

A three-dimensional Fourier synthesis, calculated on the assumption that the silver atom determined all the phases, confirmed and extended the conclusions reached from consideration of the projection. The electron density for the carbons appeared as an almost perfectly symmetrical torus around the axes; this was one indication that the structure involves more than a simple twofold disorder, since twofold disorder would be expected to produce some non-uniformity in the ring and perhaps even distinct peaks. There was no indication of peaks around the chlorine at distances appropriate for the perchlorate oxygens. Instead, a rather low electron density was spread over a shell surrounding the chlorine and was actually lower along the diagonals of the unit cell than elsewhere. The oxygen atoms would be expected to lie along these diagonals in an ordered structure or a structure with even twofold disorder. Prominent diffraction rings surrounding the position of the silver atom indicated the need for back-shift corrections.

A number of experiments with various trial structures and Fourier syntheses based upon them gave no clear criteria for choice of one structure over another. Fourier syntheses corresponding to a number of non-centrosymmetric structures, including some with the sterically very unreasonable $\bar{4}$ axis for the dioxane molecule, showed peaks corresponding closely to the positions of the atoms used in the phasing calculation. Consequently it appeared that the best approach to the solution of this structural problem involved the detailed comparison of the observed amplitudes with those calculated for several different structures, and this approach was therefore adopted. Two non-centrosymmetric and ten centrosymmetric structures were tested and one of the latter was found to give significantly better agreement than all the others, and in addition to be entirely reasonable chemically. It also accorded well with all features of the centrosymmetric Fourier synthesis.

The non-centrosymmetric structures were based on *P*$\bar{4}$3*m* and included the perchlorate oxygen atoms in ordered positions with the dioxane carbon atoms either ordered or in twofold disordered positions. The ordered positions for the carbon atoms corresponded to the almost impossible $\bar{4}$ configuration of the dioxane molecule. Even with revised temperature factor and scale-factor parameters these structures gave comparatively poor agreement and were not considered further.

The ten centrosymmetric structures tested, all of which necessarily involved some disorder, corresponded to five possible arrangements of the dioxane molecules and two possible orientations of the perchlorate groups. The contributions from the atoms in these different possible arrays were combined with the contributions of the silver and chlorine atoms, which are uniquely determined. The following tabulation describes the various orientations which were tried:

(1) The perchlorate oxygens were assumed to be 1·44 Å from the chlorine and to be:

(*a*) Rotating, or randomly distributed over a shell surrounding the chlorine.

(*b*) Along the body diagonals with a twofold disorder.

(2) The dioxane molecules were assumed to be:

(*a*) Rotating around the axes. The carbon was assigned a radius of rotation of 1·17 Å around the point 0, 0, 0·410 and the oxygen a radius of rotation of 0·67 Å around the point 0, 0, 0·333.

(*b*) Rotating around the axes. The carbon was assigned a radius of rotation of 1·17 Å around the point 0, 0, 0·410 and the oxygen was placed on the axis at 0, 0, 0·333.

(*c*) In a fourfold disordered arrangement. The carbons were disordered about the 001 planes at 0·031, 0·150 and 0·400 and other positions related as are the general positions of *Pm*3*m*. The oxygens were on the axes at 0, 0, 0·333.

(*d*) In a fourfold disordered arrangement. The carbons were disordered about the 110 planes at 0·084, 0·128 and 0·400 and other positions related as are the general positions of *Pm*3*m*. The oxygens were on the axes at 0, 0, 0·333.

(*e*) In a fourfold disordered arrangement. The carbons were 1·17 Å from the cell edge on the 110 plane with typical coordinates 0·108, 0·108 and 0·400. The oxygens were 0·67 Å from the cell edge on the 110 planes with typical coordinates 0·062, 0·062 and 0·333. The other positions for both the carbons and oxygens were related as are the positions (*m*) of *Pm*3*m*.

The temperature factor used in all calculations at this stage was 3·4 Å^2. For the *n*-fold disordered structures, 1/*n*th part of an atom was put into each position for the structure-factor calculation.

The contributions of the rotating groups were not calculated directly on SWAC because no special routines for these calculations had yet been written. Instead, the contributions of atoms situated at the centers of rotation were calculated in the usual way with SWAC and were then modified by means of appropriate functions with a desk calculator. The effective scattering power of a rotating perchlorate group is $f_{\text{Cl}}+4f_{\text{O}}\ (\sin rs/rs)$, where $s = 4\pi \sin \theta/\lambda$ (James, 1950). The radius of the spherical shell (r) was assumed to be 1·44 Å, which is the average distance found in other perchlorates (Prosen & Trueblood, 1956). The perchlorate group as a whole was centered at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The scattering power of the rotating carbon and oxygen atoms of the dioxane was approximated by a circular torus within which the electron distribution was Gaussian. The modifying function for this purpose was the zero-order Bessel function for which the argument was $2\pi r|\mathbf{h}| \sin \psi$, in which r is the radius of rotation, **h** the reciprocal-lattice vector, and ψ the angle between the axis of rotation and **h** (Milberg & Lipscomb, 1951; Lipscomb, 1955). The radii used were 1·17 Å for the carbon atoms and 0·67 Å for the oxygen atoms; this radius for the oxygens

Table 2*. *Comparison of* $|F_o|$ *and* $|F_c|$ *for different models*

		2(*a*)		2(*b*)		2(*c*)		2(*d*)		2(*e*)	
h k l	$\lvert F_o\rvert$	1(*a*)	1(*b*)	1(*a*)	1(*b*)	1(*a*)	1(*b*)	1(*a*)	1(*b*)	1(*a*)	1(*b*)
1 0 0	251	411	417	431	437	438	444	435	441	401	407
2 0 0	562	863	837	931	905	915	899	898	872	848	822
4 0 0	338	180	83	302	205	343	246	229	132	41	56
5 0 0	224	138	233	252	341	316	405	198	286	55	144
6 0 0	282	192	147	285	239	334	289	244	199	103	58
7 0 0	152	93	94	157	158	164	165	123	124	4	5
4 1 0	204	133	201	164	232	147	215	160	228	107	175
5 1 0	282	267	203	295	231	297	233	302	238	295	231
3 3 0	387	320	372	456	508	427	479	472	523	355	407
4 3 0	228	130	169	216	255	187	226	239	278	161	200
5 3 0	241	190	217	271	298	271	298	269	296	188	215
4 4 0	256	241	304	257	310	210	273	316	379	343	406
5 4 0	118	83	37	94	48	75	29	112	66	135	89
6 4 0	172	171	189	204	222	175	193	230	248	226	244
5 5 0	141	149	186	154	191	168	205	129	166	131	168
5 1 1	126	178	229	121	172	100	141	157	208	264	315
6 1 1	199	209	260	170	221	149	200	202	253	272	323
5 4 1	156	184	216	135	167	144	176	125	157	170	202
6 6 1	55	40	32	68	60	51	43	86	78	37	29
2 2 2	142	278	311	215	248	169	202	214	247	317	350
3 3 3	258	142	149	274	281	240	247	280	297	175	182
R†		0·281	0·341	0·117	0·258	0·154	0·206	0·181	0·320	0·435	0·463

* Structure factors are ten times the absolute value. See text for description of models.

† *R* evaluated for these planes with omission of (100) and (200); see text.

corresponded not only to their distance from the carbon plane in dioxane but also to a position such that their unshared electrons were favorably situated for bonding with the silver ion.

Table 2 comprises a list of the observed structure factors and those calculated from the several different centrosymmetric models for some of the critical reflections. Model 2(*b*)1(*a*), which corresponds to a rotating perchlorate group and a rotating dioxane molecule with the oxygen atoms on the axes, shows appreciably better agreement than the others. The overall reliability index for this structure at this stage of refinement was 0·191; when (200), (110), and (100) were omitted, R was 0·157. The calculated structure factors for these three planes are appreciably too large for all assumed structures. Presumably all are affected by secondary extinction; the first two are the strongest reflections observed and (100), which is also strong, was obscured on the intensity photographs by a streak of white radiation, so that its observed amplitude is not very reliable.

The phases of all but two planes are determined by the silver ion for all centrosymmetric structures tested. The two unique planes are (111), which has a negative sign for all the structures, and (551), which is positive in most but negative in a few. A three-dimensional Fourier summation was calculated with the phase angles obtained from structure 2(*b*)1(*a*). The negative contribution of (111) caused a considerable increase in the electron density around the chlorine, although the shell still was not uniform. Otherwise the density was essentially the same as that calculated with all signs positive. The apparent non-uniformity of the shell appeared to be caused by the extinction errors, for a Fourier summation based upon the calculated amplitudes for (100), (200), and (110) and the observed amplitudes for all other planes gave a density distribution essentially identical with the previous ones except that the shell around the chlorine was almost spherically symmetrical.

The procedure described by Hamilton (1955) was used to find approximate corrections to the temperature factors of the silver and chlorine atoms from a difference Fourier map. The temperature factor for the silver atom appeared to be approximately correct; that for the chlorine atom was raised to 5·0 Å^2, and this value was used also for the oxygen atoms of the dioxane molecule in the calculation of a further set of structure factors. The overall reliability index decreased to 0·151; omission of (100), (200) and (110) gave 0·116.

Finally, approximate absorption corrections were made on the assumption that the absorption by the nearly spherical crystal varied only with $\sin\theta$, and the corrected amplitudes were used in the evaluation of a new scale factor and overall temperature factor. A modified least-squares calculation in which the parameters of the rotating groups were assumed to be correct and were not refined was then made. The final parameters obtained are listed in Table 3. The corresponding structure factors (Table 4) gave an overall reliability index of 0·132; omission of (100), (200), and (110) gave $R = 0{\cdot}094$.

Table 3. *Final parameters*

Atom	x	y	z	B_{11} (Å^2)	B_{22} (Å^2)	B_{33} (Å^2)
Ag	0·000	0·000	0·000	3·8	3·8	3·8
Cl	0·500	0·500	0·500	5·1	5·1	5·1
O_D	0·321	0·000	0·000	4·5	10·0	10·0
C_D†	0·410	0·000	0·000	(3·4)*	(3·4)*	(3·4)*
O_{Cl}†	0·500	0·500	0·500	(3·4)*	(3·4)*	(3·4)*

* These were assumed at a comparatively early stage (see text) and not refined.

† The positions for C_D and O_{Cl} represent the centers of rotation, with radii 1·17 and 1·44 Å respectively.

Discussion of the structure

Fig. 1 shows the electron density $\varrho(x, y, z)$ in superposed sections parallel to (001) which pass near the maxima of the peaks. The first contour is at the 1 e.Å^{-3} level. Each successive contour is drawn at an interval of 1 e.Å^{-3} for the dioxane oxygen, 2 e.Å^{-3} for the chlorine and 5 e.Å^{-3} for the silver. The 1·5 e.Å^{-3} contour has been included (dashed) in order to define the rotating groups more clearly.

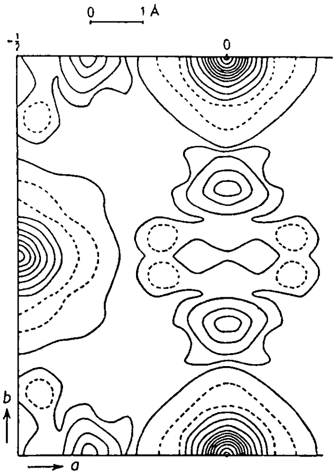

Fig. 1. Superposed Fourier sections parallel to (001). The lowest contour level is for 1 e.Å^{-3}; that for 1·5 e.Å^{-3} is dashed. The contour interval is 1 e.Å^{-3} for the dioxane oxygen atoms, 2 e.Å^{-3} for the chlorine atom, and 5 e.Å^{-3} for the silver atoms.

Fig. 2 is a drawing of a portion of the structure. The silver ions, at the corners of the unit cube, are surrounded by a regular octahedron of dioxane oxygen atoms at a distance of 2·46 Å. This distance is in good agreement with those found in other colorless crystals containing silver–oxygen coordination (Donohue & Shand, 1947) and indicates that there is negligible covalent character in the bond (Pitzer & Hildebrand, 1942).

Table 4*. *Final values of* $|F_o|$ *and* $|F_c|$

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
1	0	0	265	438	7	6	0	50	45	9	2	2	51	46
2	0	0	569	885	1	1	1	258	281	3	3	2	345	303
3	0	0	350	407	2	1	1	355	339	4	3	2	149	142
4	0	0	330	261	3	1	1	284	324	5	3	2	182	164
5	0	0	216	196	4	1	1	299	261	6	3	2	126	114
6	0	0	264	215	5	1	1	121	142	7	3	2	107	103
7	0	0	138	137	6	1	1	185	171	8	3	2	50	48
8	0	0	83	103	7	1	1	95	71	9	3	2	50	55
9	0	0	66	63	8	1	1	73	73	4	4	2	182	201
1	1	0	323	599	9	1	1	61	48	5	4	2	85	62
2	1	0	233	238	2	2	1	168	144	6	4	2	131	136
3	1	0	413	491	3	2	1	332	354	7	4	2	54	50
4	1	0	200	178	4	2	1	145	140	8	4	2	64	56
5	1	0	272	257	5	2	1	191	183	5	5	2	112	108
6	1	0	132	108	6	2	1	121	96	6	5	2	74	73
7	1	0	167	166	7	2	1	122	121	7	5	2	71	75
8	1	0	48	55	8	2	1	51	47	8	5	2	36	35
9	1	0	73	68	9	2	1	69	64	6	6	2	79	73
2	2	0	355	395	3	3	1	316	287	7	6	2	45	42
3	2	0	289	279	4	3	1	268	270	3	3	3	246	218
4	2	0	263	225	5	3	1	100	92	4	3	3	232	246
5	2	0	129	113	6	3	1	181	179	5	3	3	113	87
6	2	0	225	202	7	3	1	76	64	6	3	3	163	159
7	2	0	109	97	8	3	1	74	73	7	3	3	60	62
8	2	0	83	87	9	3	1	45	47	8	3	3	61	64
9	2	0	53	49	4	4	1	123	115	4	4	3	117	115
3	3	0	378	388	5	4	1	144	138	5	4	3	138	131
4	3	0	219	194	6	4	1	91	85	6	4	3	84	79
5	3	0	227	207	7	4	1	91	80	7	4	3	77	73
6	3	0	148	141	8	4	1	46	42	8	4	3	30	38
7	3	0	124	128	9	4	1	40	54	5	5	3	77	65
8	3	0	54	47	5	5	1	60	41	6	5	3	97	91
9	3	0	57	59	6	5	1	92	107	7	5	3	57	53
4	4	0	243	245	7	5	1	45	52	6	6	3	54	49
5	4	0	109	90	8	5	1	46	51	7	6	3	40	50
6	4	0	155	169	6	6	1	47	57	4	4	4	146	149
7	4	0	63	63	7	6	1	51	61	5	4	4	68	56
8	4	0	66	63	2	2	2	142	202	6	4	4	91	86
9	4	0	17	39	3	2	2	172	177	7	4	4	47	46
5	5	0	128	125	4	2	2	188	198	8	4	4	35	46
6	5	0	81	89	5	2	2	99	67	5	5	4	86	91
7	5	0	72	82	6	2	2	197	180	6	5	4	41	53
8	5	0	28	39	7	2	2	83	73	7	5	4	52	59
6	6	0	79	92	8	2	2	82	77	6	6	4	53	53

* Structure factors are ten times the absolute value.

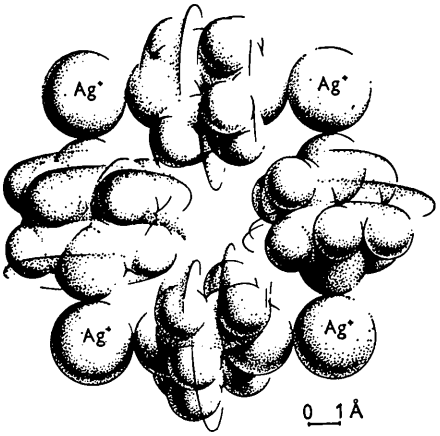

Fig. 2. A section through the structure at $x = 0$. The dioxane molecules are represented in various rotational orientations. The perchlorate ion, centered at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, extends to within about 1 Å of the plane $x = 0$.

Standard ionic and van der Waals radii (Pauling, 1940) were used to estimate the effective sizes of the various groups. The overall effective length of the dioxane molecule is about 5·3 Å; the envelope of its rotation has a maximum diameter of about 6·0 Å although the average is appreciably less because the molecule is only 4–4·5 Å thick. Even in the plane of maximum extension, the diameter probably decreases somewhat in the region between the methylene groups, and it is just in this region that the perchlorate group in the center of the unit cell approaches the edges most closely. Thus to some extent the dioxane is contoured favorably to fit the nearly spherical perchlorate ion. The perchlorate ion itself probably has an effective diameter of a little less than 5·5 Å; even if it were a sphere with the chlorine–oxygen vector as radius it would have a diameter of no more than about 5·6 Å.

The packing is thus comparatively efficient. The dioxane molecules are nearly in contact with each other in the section illustrated, and are in fairly close contact with the perchlorate ion also; the maximum radii of each group indicate slight overlapping, which suggests minimal synchronization of rotation. Although the silver ion might, by virtue of its charge, tend to orient the oxygen atoms of the perchlorate ion, this silver–oxygen distance is at the very least slightly more than 5 Å, and furthermore there is some shielding by the dioxane molecules. Consequently it is not surprising that the perchlorate ion is not found to be precisely oriented. Because packing considerations suggest that there is very nearly free rotation of both the dioxane molecules and the perchlorate ion, this possibility seems more likely to us than the presence of essentially stationary but randomly oriented groups. Experiments at low temperatures might permit a clear distinction to be made.

The temperature factors of the oxygen atoms of the dioxane molecule are very anisotropic. If the logical assumption is made that the dioxane molecule is comparatively rigid, the oxygen temperature factor in the direction of the silver atoms would be expected to be of the same order of magnitude as that for the silver atom. Experimentally, B is 4·5 Å^2 for the oxygen atom in the direction of the silver and 3·8 Å^2 for the silver. On the other hand, a larger temperature factor would be expected for each oxygen atom in directions normal to the silver–oxygen line since the forces holding it in these directions are comparatively weak. Among the possibilities tested, the best agreement is obtained with B, as normally defined, equal to about 10 Å^2 in these directions, which corresponds to a mean amplitude of vibration of about 0·36 Å; many large discrepancies occur if it is assumed that the oxygen atoms rotate with a radius of about 0·67 Å.

Although it is not entirely clear why this comparatively stable complex is formed, certainly the weakly bidentate nature of dioxane plays a large role, since it permits this molecule to act as a link tying the cubic lattice of silver ions together in an efficiently packed structure. The silver ion–oxygen bond presumably arises primarily from ion–dipole forces and thus need not be localized or directional in character; consequently the vibration, or possible small-radius rotation, of the dioxane oxygen atoms does not necessarily materially weaken the silver–oxygen bond.

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