

The Crystal Structure of One Pseudo-Diels–Alder Dimer of Norbornadiene

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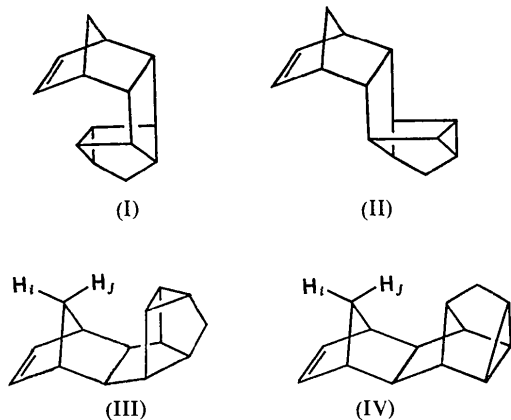
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$\text{AgNO}_3\text{C}_{14}\text{H}_{16}$, monoclinic, $P2_1/c$; $a=17.554$ (9), $b=6.908$ (4), $c=11.031$ (5) Å, $\beta=103.10^\circ$, $Z=4.0$, $R=9.1$. The stereochemistry is identified. Silver is shown to be equidistant from two carbon atoms involved in the double bond with short distances of 2.31 and 2.33 Å.

Introduction

The photochemical dimerization of norbornadiene using $\text{Ni}(\text{CO})_4$ as a catalyst has been found to produce two pseudo-Diels–Alder dimers which may have any one of the following structures (Voecks, Jennings, Smith & Coughlan, 1972).



The stereochemistry of (I) and (II) has been assigned by Katz, Carnahan & Boeckle (1967). The crystal structure of (III) was undertaken in order to establish unambiguously the stereochemistry of one of the remaining compounds and also to provide information which would make it possible to correlate the actual structure with its NMR spectrum.

Experimental

A saturated silver nitrate solution was added to (III). The resulting precipitate was washed with water and recrystallized from absolute ethanol. Since these clear, colorless crystals were not stable in the presence of water vapor, it was necessary to mount them inside Lindemann glass capillaries. Preliminary Weissenberg photographs indicated monoclinic symmetry with extinctions $0k0$, $k \neq 2n$ and $h0l$, $l \neq 2n$ which uniquely defined the space group as $P2_1/c$.

Precise unit-cell dimensions were determined from a

Table 1. Crystal data

$\text{AgNO}_3\text{C}_{14}\text{H}_{16}$	
$a=17.554$ (9) Å	
$b=6.908$ (4)	$\beta=103.10$ (3)°
$c=11.031$ (5)	$Z=4$
Space group $P2_1/c$	
$D_o=1.78$	$D_c=1.81$ g cm ⁻³
$\mu(\text{Mo } K\alpha)=15.15$ cm ⁻¹	

least-squares refinement of 15 independent measurements taken on a G.E. XRD-5 diffractometer using $\text{Mo } K\alpha$ radiation and a scintillation counter as a detector. Crystal data are listed in Table 1.

The crystal which was used for both the determination of lattice parameters and for the first half of the data collection was mounted along b and was bound by $\{100\}$, $\{001\}$ and $\{011\}$. Its approximate dimensions were $0.1 \times 0.5 \times 0.5$ mm.

A unique data set was collected by the θ - 2θ scan technique using 60 s scans at 2° min^{-1} and counting backgrounds for 10 s on either side of the peak. Three standard reflexions were measured every 50 reflexions. During the course of the data collection, the crystal gradually turned brown and the standard intensities decreased. Approximately halfway through the data collection, the standards had decreased by 20%. At this point a new crystal bound by the same form of planes and of approximately the same size was used to finish data collection. In this manner, 1181 intensities below a 2θ of 40° were measured and 841 of these were considered observed based on the criteria $I > 2\sigma(I)$. The remaining 340 were given zero weight and were not used in the refinement.

The data were corrected for Lorentz and polarization factors in the usual manner. A correction for absorption was made using the method of deMeulenaer & Tompa (1965); transmission coefficients varied from 0.83 to 0.97. Weights were calculated according to the method of Stout & Jensen (1968): $w = \{1/4LpI[\sigma^2(I) + (0.05I)^2]\}^{-1}$. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1962) for all atoms other than H; both real and imaginary terms were applied to Ag. Hydrogen scattering factors were from Stewart, Davidson & Simpson (1965). No correction for extinction was applied.

Table 2. *Positional and thermal parameters*

All values for non-hydrogen atoms have been multiplied by 10^4 . The form of anisotropic temperature factor is $\exp[-(\sum_{i=1,3}\sum_{j=1,3}h_ih_j\beta_{ij})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	650.8 (5)	836.9 (10)	3999.0 (6)	70.4 (4)	338.1 (22)	144.5 (9)	-15.3 (9)	7.7 (4)	-5.6 (12)
C(1)	1876 (6)	1256 (12)	5293 (8)	65 (5)	244 (26)	129 (10)	15 (11)	3 (6)	40 (13)
C(2)	1437 (5)	2695 (15)	5559 (7)	56 (5)	341 (30)	102 (9)	-6 (10)	17 (5)	12 (13)
C(3)	2505 (6)	2073 (13)	4701 (7)	69 (5)	265 (25)	112 (9)	24 (10)	31 (6)	13 (13)
C(4)	1774 (5)	4537 (11)	5149 (7)	66 (5)	217 (24)	105 (9)	36 (9)	0 (5)	10 (12)
C(5)	3041 (6)	3045 (12)	5841 (6)	61 (5)	281 (24)	90 (8)	27 (10)	9 (5)	34 (12)
C(6)	2545 (5)	4744 (12)	6139 (6)	54 (4)	245 (23)	88 (8)	14 (9)	13 (5)	8 (11)
C(7)	2046 (5)	3783 (11)	4021 (6)	58 (4)	285 (24)	91 (8)	11 (9)	19 (5)	1 (12)
C(8)	3819 (6)	4044 (13)	5713 (7)	53 (5)	329 (25)	133 (10)	58 (11)	18 (5)	4 (14)
C(9)	3103 (5)	6498 (13)	6155 (7)	57 (5)	304 (26)	109 (9)	41 (9)	8 (5)	-61 (12)
C(10)	3729 (6)	5407 (13)	4613 (7)	58 (5)	359 (30)	117 (9)	1 (11)	20 (5)	11 (14)
C(11)	3248 (5)	7035 (12)	4919 (8)	52 (5)	260 (25)	137 (11)	16 (10)	13 (5)	8 (13)
C(12)	4108 (7)	7293 (15)	5060 (9)	76 (7)	420 (36)	164 (12)	-25 (12)	32 (7)	74 (16)
C(13)	4506 (6)	7065 (16)	6415 (9)	57 (6)	457 (34)	204 (13)	-20 (11)	28 (6)	-30 (17)
C(14)	3898 (6)	5649 (17)	6700 (9)	65 (6)	431 (33)	97 (10)	10 (12)	-4 (6)	26 (17)
N(1)	-798 (7)	2652 (13)	2734 (8)	56 (5)	351 (28)	129 (10)	31 (11)	5 (6)	-47 (13)
O(1)	-711 (4)	1437 (10)	3576 (6)	81 (4)	419 (20)	163 (8)	2 (8)	35 (5)	41 (10)
O(2)	-1430 (5)	3288 (11)	2260 (6)	68 (4)	483 (23)	212 (10)	52 (8)	16 (5)	-40 (11)
O(3)	-202 (5)	3138 (11)	2352 (6)	63 (4)	509 (25)	185 (9)	-11 (9)	20 (5)	82 (11)

Table 2 (cont.)

Hydrogen atom positional parameters have been multiplied by 10^3 . Isotropic temperature factors, *B*, are given.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	192 (3)	26 (7)	568 (5)	3.7 (12)
H(2)	108 (3)	266 (7)	608 (4)	3.6 (13)
H(3)	287 (4)	113 (8)	412 (5)	5.6 (16)
H(4)	155 (3)	546 (8)	499 (5)	4.7 (14)
H(5)	318 (3)	199 (8)	654 (4)	4.2 (13)
H(6)	253 (4)	423 (10)	697 (6)	7.9 (19)
H(7)	173 (4)	324 (10)	336 (5)	6.2 (17)
H(8)	238 (3)	452 (7)	370 (4)	2.9 (11)
H(9)	418 (3)	326 (7)	580 (4)	2.9 (11)
H(10)	296 (3)	733 (8)	658 (4)	3.8 (13)
H(11)	369 (4)	474 (10)	381 (6)	7.4 (19)
H(12)	276 (4)	780 (8)	424 (5)	5.0 (15)
H(13)	427 (5)	810 (11)	464 (6)	4.5 (22)
H(14)	499 (5)	678 (13)	657 (8)	6.2 (26)
H(15)	442 (4)	840 (10)	686 (6)	4.7 (18)
H(16)	395 (4)	508 (9)	734 (6)	3.4 (19)

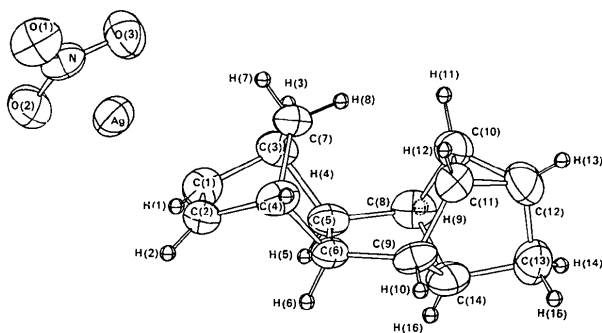


Fig. 1. ORTEP drawing illustrating the asymmetric portion of the unit cell. Thermal ellipsoids have been scaled to include 30% probability; hydrogen atoms have been assigned an isotropic temperature factor of 1.0 for clarity.

Structure determination and refinement

A three-dimensional Patterson map was calculated which clearly indicated the position of the Ag atom. Its position was refined by several cycles of block-diagonal least-squares calculations; the rest of the non-hydrogen atoms were located from several successive three-dimensional Fourier syntheses. The structure was then refined isotropically by full-matrix least squares, minimizing $\sum w\Delta F^2$ to an *R* value ($R = \sum |F_o - F_c| / \sum |F_o|$) of 10.2%. Further refinements of both positional and anisotropic thermal parameters reduced *R* to 5.3%. A difference synthesis calculated at this point revealed the position of each H atom. The structure was then refined treating the vibration of nonhydrogen atoms anisotropically and the vibration of H atoms isotropically until the largest shift divided by the error was 0.07. The final *R* was 3.3% while the weighted *R_w* ($R_w = [\sum w\Delta F^2]^{1/2} / [\sum wF_o^2]^{1/2}$) was 4.2%. *S*, the standard deviation of an observation of unit weight ($S = [\sum w\Delta F^2 / (m - n)]^{1/2}$ where *m* is the number of observations and *n* is the number of parameters) was calculated to be 0.91. The *R* value for both the observed and unobserved data was 9.1%. The largest peak on the final difference Fourier was 0.3 e Å⁻³ while the most negative area was -0.3 e Å⁻³.*

* The computer programs used were the following: *NRC-2*, data reduction program written by F. R. Ahmed and C. P. Sanderson; *NRC-8*, Fourier program, and *NRC-10*, block diagonal least squares, written by F. R. Ahmed, National Research Council, Ottawa, Ontario, Canada; *ORFLS*, the full-matrix least-squares program written by W. R. Busing, K. O. Martin and H. S. Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn.; and *ORTEP*, written by C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tenn. These have been adapted for the XDS Sigma-7 computer. The rest of the programs were written by G. D. Smith, E. L. Enwall, and C. N. Caughlan, Montana State University, Bozeman, Montana.

Table 3. Bond distances (Å)

Ag—C(1)	2.31 (1)	C(8)—C(10)	1.52 (1)
Ag—C(2)	2.33 (1)	C(8)—C(14)	1.54 (1)
C(1)—C(2)	1.33 (1)	C(8)—H(9)	0.82 (5)
C(1)—C(3)	1.51 (2)	C(9)—C(11)	1.49 (1)
C(1)—H(1)	0.80 (6)	C(9)—C(14)	1.51 (1)
C(2)—C(4)	1.52 (1)	C(9)—H(10)	0.82 (6)
C(2)—H(2)	0.94 (5)	C(10)—C(11)	1.49 (1)
C(3)—C(5)	1.54 (1)	C(10)—C(12)	1.50 (1)
C(3)—C(7)	1.53 (1)	C(10)—H(11)	0.99 (7)
C(3)—H(3)	1.20 (6)	C(11)—C(12)	1.49 (2)
C(4)—C(6)	1.54 (1)	C(11)—H(12)	1.13 (6)
C(4)—C(7)	1.52 (1)	C(12)—C(13)	1.51 (1)
C(4)—H(4)	0.75 (6)	C(12)—H(13)	0.82 (8)
C(5)—C(6)	1.54 (1)	C(13)—C(14)	1.53 (2)
C(5)—C(8)	1.56 (1)	C(13)—H(14)	0.85 (9)
C(5)—H(5)	1.05 (6)	C(13)—H(15)	1.07 (7)
C(6)—C(9)	1.56 (1)	C(14)—H(16)	0.80 (6)
C(6)—H(6)	0.99 (7)	N—O(1)	1.24 (1)
C(7)—H(7)	0.89 (6)	N—O(2)	1.20 (1)
C(7)—H(8)	0.91 (5)	N—O(3)	1.26 (1)

Table 4. Bond angles (°)

C(2)—C(1)—C(3)	109.4 (8)	C(11)—C(9)—H(10)	119. (4)
C(2)—C(1)—H(1)	121. (4)	C(14)—C(9)—H(10)	115. (4)
C(3)—C(1)—H(1)	124. (4)	C(8)—C(10)—C(11)	104.4 (7)
C(1)—C(2)—C(4)	106.1 (8)	C(8)—C(10)—C(12)	108.6 (8)
C(1)—C(2)—H(2)	128. (3)	C(8)—C(10)—H(11)	114. (4)
C(4)—C(2)—H(2)	124. (3)	C(11)—C(10)—C(12)	60.0 (6)
C(1)—C(3)—C(5)	100.4 (7)	C(11)—C(10)—H(11)	129. (4)
C(1)—C(3)—C(7)	98.3 (7)	C(12)—C(10)—H(11)	130. (4)
C(1)—C(3)—H(3)	124. (3)	C(9)—C(11)—C(10)	104.0 (7)
C(5)—C(3)—C(7)	102.7 (7)	C(9)—C(11)—C(12)	108.2 (8)
C(5)—C(3)—H(3)	112. (3)	C(9)—C(11)—H(12)	117. (3)
C(7)—C(3)—H(3)	116. (3)	C(10)—C(11)—C(12)	60.2 (6)
C(2)—C(4)—C(6)	101.9 (7)	C(10)—C(11)—H(12)	126. (3)
C(2)—C(4)—C(7)	99.9 (7)	C(12)—C(11)—H(12)	127. (3)
C(2)—C(4)—H(4)	124. (4)	C(10)—C(12)—C(13)	107.9 (9)
C(6)—C(4)—C(7)	102.9 (6)	C(10)—C(12)—H(13)	126. (6)
C(6)—C(4)—H(4)	115. (4)	C(10)—C(12)—C(11)	59.8 (6)
C(7)—C(4)—H(4)	110. (4)	C(11)—C(12)—C(13)	108.7 (9)
C(3)—C(5)—C(6)	103.6 (7)	C(11)—C(12)—H(13)	120. (6)
C(3)—C(5)—C(8)	120.1 (7)	C(13)—C(12)—H(13)	119. (6)
C(3)—C(5)—H(5)	107. (3)	C(12)—C(13)—H(14)	116. (6)
C(6)—C(5)—C(8)	103.3 (7)	C(14)—C(13)—H(14)	121. (6)
C(6)—C(5)—H(5)	115. (3)	C(12)—C(13)—C(14)	94.7 (8)
C(8)—C(5)—H(5)	108. (3)	C(12)—C(13)—H(15)	106. (4)
C(4)—C(6)—C(5)	103.1 (6)	C(14)—C(13)—H(15)	106. (4)
C(4)—C(6)—C(9)	122.0 (7)	H(14)—C(13)—H(15)	110. (7)
C(4)—C(6)—H(6)	115. (4)	C(8)—C(14)—C(13)	105.7 (8)
C(5)—C(6)—C(9)	102.2 (6)	C(8)—C(14)—H(16)	104. (5)
C(5)—C(6)—H(6)	93. (4)	C(8)—C(14)—C(9)	94.1 (8)
C(9)—C(6)—H(6)	115. (4)	C(9)—C(14)—C(13)	107.1 (8)
C(3)—C(7)—H(7)	104. (4)	C(9)—C(14)—H(16)	117. (5)
C(3)—C(7)—H(8)	108. (3)	C(13)—C(14)—H(16)	124. (5)
C(3)—C(7)—C(4)	95.2 (6)	O(1)—N—O(2)	121.5 (10)
C(4)—C(7)—H(7)	124. (4)	O(2)—N—O(3)	120.9 (10)
C(4)—C(7)—H(8)	119. (3)	O(1)—N—O(3)	117.5 (9)
H(7)—C(7)—H(8)	105. (5)		
C(5)—C(8)—C(10)	114.3 (7)		
C(5)—C(8)—C(14)	101.2 (7)		
C(5)—C(8)—H(9)	111. (3)		
C(10)—C(8)—C(14)	95.5 (7)		
C(10)—C(8)—H(9)	116. (4)		
C(14)—C(8)—H(9)	117. (4)		
C(6)—C(9)—C(11)	114.9 (7)		
C(6)—C(9)—C(14)	103.0 (7)		
C(6)—C(9)—H(10)	106. (4)		
C(11)—C(9)—C(14)	97.3 (7)		

Discussion

The final positional and thermal parameters along with their standard deviations are listed in Table 2.* Fig. 1 is an *ORTEP* drawing illustrating the asymmetric portion of the unit cell; distances in the organic molecule and the nitrate ion are in Table 3, bond angles in Table 4.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31375 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

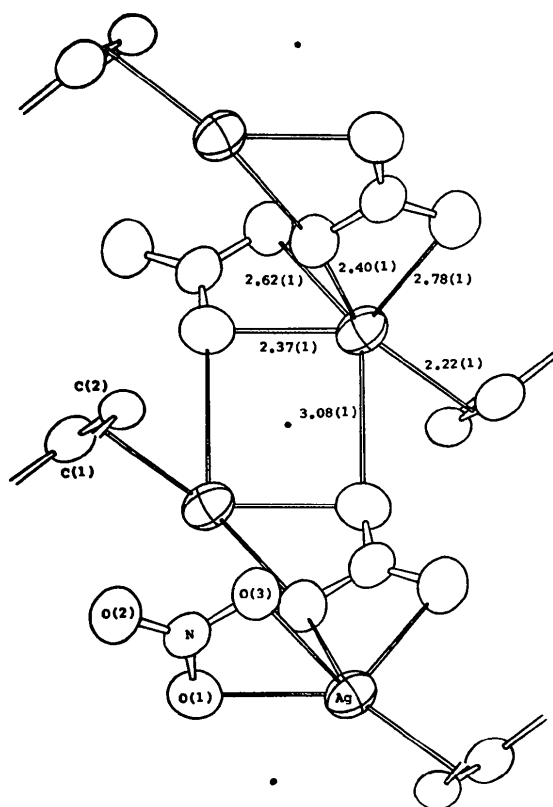


Fig. 2. *ORTEP* drawing to illustrate the interactions between the silver ion, the nitrate ions and the doubly bonded portion of the organic molecule. Small black circles are centers of inversion. The *b* axis is perpendicular to the plane of the paper, the *a* axis is nearly horizontal, while the *c* axis is vertical.

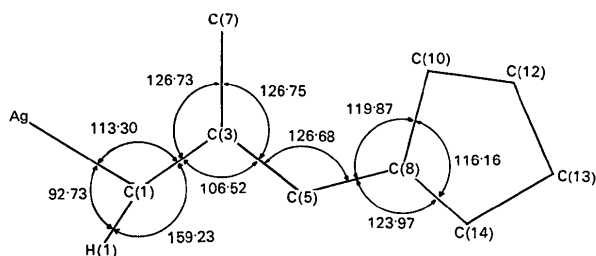


Fig. 3. Dihedral angles in the organo-silver complex. The complex is viewed perpendicular to the pseudo-mirror plane of the molecule.

Table 5. *Equations of planes*

The equation for the plane is $Ax + By + Cz - D = 0$ where A , B , and C are direction cosines, D is the perpendicular distance from the plane to the origin, and Σ is the sum of the squares of the deviations of the atoms from the least-squares plane. The orthogonal coordinate system from which these values are calculated is defined by x along \mathbf{a} , y in the \mathbf{ab} plane, and z along \mathbf{c}^* .

	A	B	C	D	Σ
Ag—C(1)—C(2)	-0.4388	-0.5694	0.6952	2.595	
C(1)—C(2)—H(1)—H(2)	0.5899	0.3502	0.7276	5.635	0.002
C(1)—C(2)—C(3)—C(4)	0.4175	0.0877	0.9044	6.040	9.6×10^{-6}
C(3)—C(4)—C(7)	0.7827	0.5724	0.2445	4.576	
C(3)—C(4)—C(5)—C(6)	-0.5203	-0.5953	0.6123	0.568	8.6×10^{-5}
C(5)—C(6)—C(8)—C(9)	0.1622	-0.1406	0.9767	6.460	2.2×10^{-5}
C(8)—C(9)—C(10)—C(11)	0.7508	0.4795	0.4543	8.090	5.7×10^{-6}
C(10)—C(11)—C(12)	-0.0579	-0.3235	0.9444	3.160	
C(8)—C(9)—C(14)	0.5479	0.6048	-0.5763	1.052	
N—O(1)—O(2)—O(3)	0.0053	0.7433	0.6689	3.301	2.7×10^{-4}

The distances and angles between non-hydrogen atoms are about what one would expect for a molecule as highly distorted as this.

C—C single bond distances range from 1.49 to 1.57 Å. Corresponding distances and angles between non-hydrogen atoms across the pseudo-mirror plane of the molecule differ by less than three standard deviations. Distances and angles involving H are not as good as could be hoped for. These results are not too surprising since the crystal suffered from decomposition, requiring the use of two crystals to collect the data, and a heavy Ag atom was present.

Table 5 contains the equations of planes of various atoms in the asymmetric unit while Fig. 3 illustrates the dihedral angles between some of these planes. C(7), H(7) and H(8) all lie on the same side of the plane defined by the cyclopropane ring [C(10), C(11) and C(12)] with distances of 0.08, 0.60 and 0.60 Å respectively. These distances and the effect of the cyclopropane ring on the NMR spectrum have been discussed by VoECKS *et al.* (1972).

The Ag is equidistant, within two standard deviations, from C(1) and C(2), the C atoms involved in the double bond. The distances of 2.31 (1) and 2.33 (1) Å between Ag and the two C atoms are to our knowledge the shortest distances of this type reported. Values of 2.38 (1) and 2.41 (1) Å have been reported for AgNO₃-cyclononatriene (Jackson & Streib, 1967), 2.31 (5) and 2.41 (4) Å for AgNO₃-norbornadiene (Baenziger, Haight, Alexander & Doyle, 1966) and 2.46 and 2.51 Å for AgNO₃-cyclooctatetraene (Matthews & Lipscomb, 1959). The Ag atom does not lie directly over the double bond between C(1) and C(2), but is displaced 23° from the perpendicular. The distance from Ag to H(1) is 2.59 (5) Å and to H(2), 2.58 (4) Å; however, the distance to H(7) is 2.73 (7) Å and although these differences are not greatly significant, we feel that the 23° distortion is not simply due to steric interaction. Distortions of this nature, are not uncommon. In AgNO₃-cyclononatriene (Jackson & Streib, 1967) a distortion of 17° is reported while in AgNO₃-norbornadiene (Baenziger *et al.*, 1966) the distortion is 24°.

There is a rather extensive network of silver and nitrate ions lying in the (100) face of the unit cell. The silver ion has three nitrate ions and one dimer unit around it in approximately a tetrahedral configuration. There are five Ag—O distances which range from 2.366 (7) to 3.083 Å. Two of these distances are short enough to be considered to have some degree of covalency in the bonding. As can be seen from Fig. 2, the interactions between the silver and nitrate ions are rather complicated. Each silver ion interacts with three nitrate ions while each nitrate ion interacts with three different silver ions. This sort of behavior was also noted by Jackson & Streib (1967). However, each silver ion is associated with only one dimer unit.

The nitrate groups are essentially planar. The shortest bond distance between N and O is associated with the O that is farthest from any silver ion.

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