

# The Crystal and Molecular Structure of the Silver Nitrate Complex of *cis,cis,cis*-1,4,7-Cyclononatriene, $C_9H_{12}(AgNO_3)_3$

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**Abstract:** The structure of the silver nitrate  $\pi$  complex of *cis,cis,cis*-1,4,7-cyclononatriene,  $C_9H_{12}(AgNO_3)_3$ , has been determined by a three-dimensional single-crystal X-ray diffraction investigation. The complex crystallizes in space group  $R\bar{3}c$ ; cell dimensions for the triply primitive hexagonal cell are  $a = 16.258$  and  $c = 9.556$  Å at approximately  $-125^\circ$ . The cyclononatriene ring is in the crown configuration and shows little or no distortion due to the complex formation. Each silver is associated with only one ethylenic bond at divergent ends of the  $\pi$ -bonded  $p$  orbitals. The silver ions are distorted  $17^\circ$  in the direction of the *cis* hydrogens.

The structure of *cis,cis,cis*-1,4,7-cyclononatriene,  $C_9H_{12}$ ,<sup>2-4</sup> is known to have a crown configuration.<sup>5,6</sup> Silver complexes of olefins are well known<sup>7</sup> and several<sup>8-13</sup> have been investigated by X-ray diffraction techniques. The present study was undertaken to further elucidate the geometry of the nine-membered ring system and to compare the bonding in the olefin with that of its silver complex.

## Experimental Section

**Data Collection.** White needles of  $C_9H_{12}(AgNO_3)_3$  were prepared<sup>14</sup> and supplied to us by Dr. Karl Untch. Irregular single crystals approximately  $0.2 \times 0.2 \times 0.3$  mm were cleaved and mounted, the first of these with the needle axis along the goniometer head axis. Preliminary Weissenberg and precession photographs indicated a rhombohedrally centered hexagonal unit cell, the hexagonal  $c$  axis corresponding to the needle axis. The conditions for nonextinction,  $-h + k + l = 3n$  for  $hkil$  and  $l = 2n$  for  $h\bar{h}0l$ , required the space group to be  $R\bar{3}c$  or  $R\bar{3}c$ . Cell dimensions obtained from film measurements and an approximate density (by flotation) of  $2.9$  g/cm<sup>3</sup> indicated six molecules in the hexagonal unit cell. It was assumed, and later verified, that the molecule had the same symmetry,  $3m-C_{3v}$ , as its parent compound. This symmetry condition restricted the space group to  $R\bar{3}c$ , since  $R\bar{3}c$  would have required the molecule to have  $\bar{3}-C_{3i}$  or  $32-D_3$  symmetry.

Two sets of three-dimensional, low-temperature intensity data were collected: initially (a) integrated Weissenberg multiple film data, using  $Cu K\alpha$  radiation, of levels  $hki0-hki3$  and  $0kil-8kil$ , and for later refinement (b) counter-diffractometer data, collected manually with  $Mo K\alpha$  radiation on a General Electric spectrogoniometer equipped with a single-crystal orienter and scintillation counter. Threefold redundant data were measured for 483 unique film intensities and 364 unique counter intensities. The integrated films were measured with a Nonius Model I densitometer. Both sets of data were collected at low temperature using a conventional nitrogen vapor cold stream in order to reduce thermal motion and to inhibit a gradual surface decomposition of the crystals. Improved hexagonal cell dimensions, obtained by least-squares fit

with diffractometer  $2\theta$  data, were  $a = 16.258 \pm 0.005$  and  $c = 9.556 \pm 0.003$  Å at approximately  $-125^\circ$ .

**Computations.** All calculations were performed on a CDC 3600 computer. The raw data were correlated and corrected for Lorentz and polarization effects using a program written at this laboratory. Standard errors for the film intensities were based on observed deviations during film correlation with a minimum error of  $0.05I_{obsd}$  to avoid accidental agreement. Standard errors for the counter data were based on counting statistics as described by Johnson.<sup>15</sup> Cell dimensions and errors were determined using the least-squares program by Heaton, Gvildys, and Mueller.<sup>16</sup> Patterson and electron-density maps were computed using the Gvildys Fourier summation program.<sup>17</sup> The Busing and Levy full-matrix least-squares program<sup>18</sup> was used for the structure refinement, and their function and error program<sup>19</sup> was used for calculation of bond distances, angles, anisotropic parameters, and their respective standard deviations.

**Structure Determination.** The structure was solved by the heavy-atom method. The  $x$  and  $y$  silver atom coordinates were determined from a two-dimensional Patterson map calculated from  $40 hki0$  film intensities. Since there was only one silver atom in the asymmetric unit and the position of the origin along the  $c$  axis was arbitrary, we proceeded directly to a three-dimensional least-squares refinement. Two cycles, varying the silver coordinates and the absolute scale factor, decreased the residual,  $R = \sum | |F_o| - |F_c| | / \sum |F_o|$ , from 0.41 to 0.22. A three-dimensional Fourier map revealed the approximate positions of the carbon ring atoms. After two least-squares cycles refining silver and carbon coordinates, another difference map was computed and the nitrate group atoms were located. Further refinement of all coordinates (except hydrogen), scale factor, and isotropic temperature factors failed to lower  $R$  below 0.185. The relatively high value of  $R$  at this stage of refinement led us to make a correction for systematic errors in the form of artificial temperature factors. The film data were collected over an extended period of time involving more than one crystal and several interruptions in the operation of the cold stream. It was therefore suspected that the various film packs may have been exposed at somewhat different temperatures and that this would constitute the major systematic error. The original intensities were corrected according to the relation  $I_{corrected} = k_i I_{obsd} \exp(-B_i \sin^2 \theta / \lambda^2)$ , where  $I_{obsd}$ 's are the observed intensities for a given film pack,  $k_i$  is the correlation scale factor for that pack, and  $B_i$  is the individual film pack temperature factor which was fitted by least squares. Two cycles of isotropic refinement with the corrected intensities, followed by two cycles with anisotropic tempera-

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Table I. Observed and Calculated Structure Factors<sup>a</sup>

hk0		hkl		hk0		hkl		hk0		hkl		hk0		hkl									
3	0	2949	2901	859	2771	3	4	2751	2778	1539	2313	3	5	1721	1777	1063	-1424	5	11	*486	582	-453	-222
6	0	5644	5761	-2983	4928	4	4	2210	2234	1362	1771	6	5	1317	1357	1332	250	0	12	1447	1497	863	-1223
9	0	3083	3008	-1191	-2762	5	4	2622	2420	-2506	764	9	5	1465	1513	268	1489	3	12	882	820	354	739
12	0	2083	2107	-1325	-1618	6	4	875	898	-594	74	12	5	1043	1046	-850	610	1	13	672	749	368	-698
15	0	149	1464	1394	448	7	5	*233	389	-170	350	1	6	2022	2120	-595	2035						
1	1	2425	2469	-2469	0	8	5	651	894	-593	-61	4	6	1524	1550	-572	1282						
4	1	2247	2193	1061	-1919	9	5	907	902	873	227	7	6	2102	2679	-1968	-1817						
7	1	771	864	633	588	10	5	1412	1400	117	1396	10	6	704	676	252	-627						
10	1	1635	1663	36	1662	13	5	*427	409	-479	-173	2	7	2151	2204	-507	-2145						
13	1	1538	1569	-800	-1350	2	6	1846	1808	975	-1523	5	7	*358	148	147	14						
16	1	*430	407	-84	-39A	5	6	1662	1701	-1592	604	8	7	1087	1125	1035	440						
2	2	667	848	-545	0	8	6	*367	240	123	-206	0	8	937	908	707	569						
5	2	353	2983	-270	-2945	11	6	1233	1311	366	-1259	3	8	970	1002	-114	996						
8	2	1367	1330	955	-926	0	7	4418	4434	-4299	1084	6	8	871	876	-672	-563						
11	2	1511	1534	1506	293	3	7	978	1013	-433	-92A	9	8	*417	169	166	31						
14	2	657	753	-88	748	6	7	2885	2961	1002	-278A	1	9	737	677	650	-188						
3	3	2815	2703	-2703	0	9	7	1107	1170	586	1012	4	9	1580	1646	1610	-341						
6	3	2928	2917	2859	580	1	8	2597	2575	2560	275	7	9	1144	1123	-389	1054						
9	3	600	656	-461	-468	4	8	1072	1088	-204	1069	2	10	1288	1355	-1040	-869						
12	3	1648	1611	14	1611	7	8	1129	1146	-948	444	5	10	799	795	463	646						
15	3	*406	834	427	-320	10	8	727	774	-333	-698	8	10	841	817	341	-743						
4	4	*242	343	-343	0	5	9	*405	430	-324	-297	0	11	2162	2276	-1202	1846						
7	4	2530	2584	-1664	1980	8	9	*390	61	13	59	3	11	1487	1468	-1237	-790						
10	4	521	557	-327	-451	0	10	2268	2245	-1806	1333	6	11	1373	1438	-519	-1341						
13	4	1251	1276	-464	-1189	3	10	1242	1210	874	-836	1	12	874	904	894	-136						
5	5	1641	1607	-1697	0	6	10	1349	1268	-1100	0	4	12	*412	461	452	-88						
8	5	683	707	-455	-541	9	10	1098	1070	702	808	2	13	1323	1365	-360	1317						
11	5	499	457	385	-533	1	11	971	914	-619	-672	0	14	1324	1360	1322	-320						
4	6	2113	2071	2071	0	4	11	588	604	-131	-590	1	15	991	909	-878	-235						
9	6	2309	2429	-1548	1877	7	11	868	880	432	-613												
12	6	593	458	142	435	2	12	636	613	-194	-470												
7	7	1828	1891	1891	0	5	12	1469	1441	1395	361												
10	7	1716	1708	1700	167	0	13	3480	3509	1752	3040												
8	8	1447	1391	-1391	0	3	13	1123	1110	-908	639												
11	8	1038	1047	-117	-1040	1	14	*387	385	-266	-27A												
9	9	*412	236	-236	0	4	14	981	972	917	322												
						2	15	*427	437	182	-397												
						0	16	892	831	798	-231												

<sup>a</sup> The  $F_o$ 's were obtained from counter data. Columns contain values of  $h, k, 10F_o, 10|F_c|, 10A_c,$  and  $10B_c$ . Unobserved reflections are designated by an asterisk.

ture factors for the silver atom, and a final cycle refining all parameters yielded a final  $R$  of 0.118. At this point the errors in the light-atom coordinates were still large and the set of counter intensity data was collected. Starting

with the previously determined parameters, two cycles of isotropic refinement, followed by two cycles with anisotropic temperature factors for silver, yielded  $R = 0.028$  and an acceptable set of standard deviations on the light atoms. The final calculated and

observed structure factors are listed in Table I which, in addition, includes 70 unobserved intensities estimated (at the raw-data level) as half the minimum observed intensity. The unobserved data were not used in the least-squares refinements.

## Results

Atom coordinates, isotropic temperature factors, and their standard deviations are given in Table II. Interatomic distances and angles and their errors are given in Table III.

Table II. Atomic Coordinates and Isotropic Temperature Factors

Atom	$x/a_1$	$y/a_2$	$z/c$	$B, \text{Å}^2$
Ag	0.8717 (1) <sup>a</sup>	0.2823 (1)	0.2441 <sup>b</sup>	... <sup>c</sup>
C <sub>1</sub>	0.7969 (10)	0.3549 (11)	0.3657 (14)	1.08 (28)
C <sub>2</sub>	0.7306 (11)	0.2589 (11)	0.3624 (12)	1.34 (27)
C <sub>3</sub>	0.6398 (12)	0.2111 (12)	0.2741 (14)	0.87 (29)
O <sub>1</sub>	0.2868 (7)	0.3018 (8)	0.1806 (10)	2.03 (22)
O <sub>2</sub>	0.2928 (7)	0.1792 (7)	0.2521 (12)	1.46 (23)
O <sub>3</sub>	0.3825 (8)	0.2645 (8)	0.0805 (11)	2.56 (24)
N	0.3217 (8)	0.2483 (8)	0.1690 (11)	1.24 (22)

<sup>a</sup> Standard deviations are  $\times 10^4$  for coordinates and  $\times 10^2$  for  $B$ 's. <sup>b</sup> The position of the origin along the  $c$  axis is arbitrary and was chosen for convenience in computing a suitable unit in the electron-density maps. <sup>c</sup> See Table IV for the anisotropic thermal parameters for silver.

Table III. Distances and Angles for  $\text{C}_9\text{H}_{12}(\text{AgNO}_3)_3$

Bonded Distances (Å) and Angles			
C <sub>2</sub> -C <sub>3</sub>	1.532 ± 0.020	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	107.6 ± 1.1°
C <sub>3</sub> -C <sub>4</sub>	1.542 ± 0.019	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	126.4 ± 1.2°
C <sub>1</sub> -C <sub>2</sub>	1.384 ± 0.020	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	122.9 ± 1.4°
Ag <sub>1</sub> -C <sub>1</sub>	2.379 ± 0.015	Ag <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	74.5 ± 0.9°
Ag <sub>1</sub> -C <sub>2</sub>	2.411 ± 0.014	Ag <sub>1</sub> -C <sub>2</sub> -C <sub>1</sub>	71.9 ± 0.9°
N-O <sub>1</sub>	1.259 ± 0.015	O <sub>1</sub> -N-O <sub>2</sub>	117.7 ± 1.1°
N-O <sub>2</sub>	1.259 ± 0.014	O <sub>2</sub> -N-O <sub>3</sub>	121.9 ± 1.3°
N-O <sub>3</sub>	1.225 ± 0.013	O <sub>1</sub> -N-O <sub>3</sub>	120.4 ± 1.2°
Midpoint of C <sub>1</sub> -C <sub>2</sub> to Ag <sub>1</sub> 2.300 ± 0.014			
Nonbonded Distances (Å)			
C <sub>2</sub> -C <sub>4</sub>	2.480 ± 0.020	O <sub>1</sub> -O <sub>2</sub>	2.155 ± 0.016
C <sub>3</sub> -C <sub>5</sub>	3.133 ± 0.027	O <sub>1</sub> -O <sub>3</sub>	2.156 ± 0.015
Ag <sub>1</sub> -C <sub>3</sub>	3.357 ± 0.016	O <sub>2</sub> -O <sub>3</sub>	2.172 ± 0.016
Ag <sub>1</sub> -C <sub>9</sub>	3.281 ± 0.017		
Distances (Å) and Angles in Silver Environment			
Ag <sub>2</sub> -O <sub>2</sub>	2.438 ± 0.012	Ag <sub>2</sub> -O <sub>3</sub>	3.190 ± 0.011
Ag <sub>2</sub> -O <sub>3</sub>	2.927 ± 0.011	Ag <sub>2</sub> -O <sub>12</sub>	3.240 ± 0.011
Ag <sub>2</sub> -O <sub>4</sub>	2.484 ± 0.010	O <sub>2</sub> -Ag <sub>2</sub> -O <sub>4</sub>	97.7 ± 0.4°
Ag <sub>2</sub> -O <sub>5</sub>	2.771 ± 0.012	O <sub>2</sub> -Ag <sub>2</sub> -O <sub>7</sub>	111.5 ± 0.3°
Ag <sub>2</sub> -O <sub>7</sub>	2.474 ± 0.010	O <sub>4</sub> -Ag <sub>2</sub> -O <sub>7</sub>	86.3 ± 0.2°
(Midpoint of C <sub>4</sub> -C <sub>5</sub> )-Ag <sub>2</sub> -O <sub>7</sub> 109.9 ± 0.2°			
(Midpoint of C <sub>4</sub> -C <sub>5</sub> )-Ag <sub>2</sub> -O <sub>2</sub> 108.8 ± 0.2°			
(Midpoint of C <sub>4</sub> -C <sub>5</sub> )-Ag <sub>2</sub> -O <sub>4</sub> 140.1 ± 0.2°			
Distances (Å) in Nitrate Environment			
Ag <sub>2</sub> -O <sub>2</sub>	2.430 ± 0.012	Ag <sub>4</sub> -O <sub>1</sub>	2.474 ± 0.010
Ag <sub>2</sub> -O <sub>3</sub>	2.927 ± 0.011	Ag <sub>4</sub> -O <sub>3</sub>	3.190 ± 0.011
Ag <sub>3</sub> -O <sub>3</sub>	3.240 ± 0.011	Ag <sub>5</sub> -O <sub>1</sub>	2.484 ± 0.009
Ag <sub>3</sub> -O <sub>1</sub>	4.711 ± 0.010	Ag <sub>5</sub> -O <sub>2</sub>	2.771 ± 0.012
Dihedral Angles between Planes Each Defined by Three Atoms			
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> and C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>		73.0 ± 1.7°	
Ag <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub> and C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>		107.8 ± 1.5°	
Ag <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub> and C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>		106.4 ± 1.5°	
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> and $a, b$ plane		49.3 ± 0.4°	
O <sub>1</sub> -O <sub>2</sub> -O <sub>3</sub> and $a, b$ plane		42.4 ± 0.8°	
Ag <sub>2</sub> -Ag <sub>4</sub> -Ag <sub>5</sub> and O <sub>1</sub> -O <sub>2</sub> -O <sub>3</sub>		8.3 ± 1.0°	

As proposed,<sup>14</sup> the cyclononatriene ring retains the crown configuration on complex formation with silver nitrate. The rings are stacked along the threefold axes

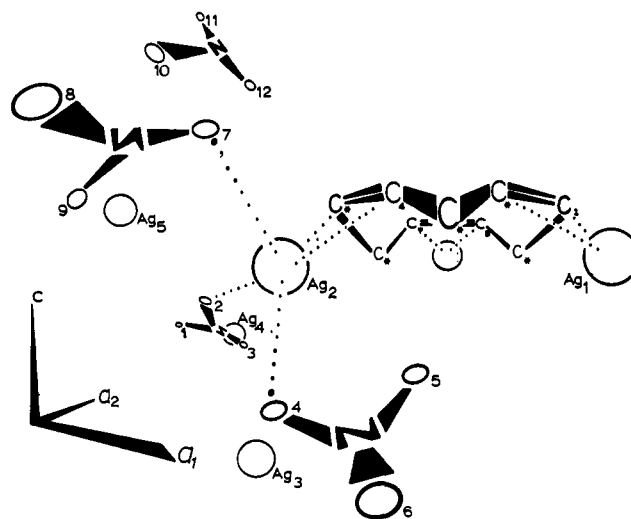


Figure 1. The environment of a silver ion ( $\text{Ag}_2$ ) showing all neighboring oxygen atoms.  $\text{Ag}_1$  and  $\text{Ag}_2$  are related by a threefold axis;  $\text{Ag}_3$ ,  $\text{Ag}_4$ , and  $\text{Ag}_5$  are related by a  $3_1$  screw axis. A  $3_2$  screw axis relates the  $\text{NO}_3$  groups 4-5-6, 7-8-9, and 10-11-12. Oxygens  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{O}_4$ ,  $\text{O}_5$ ,  $\text{O}_7$ ,  $\text{O}_9$ , and  $\text{O}_{12}$  are within 4.0 Å of the silver ion.  $\text{Ag}_2$ - $\text{O}_2$ ,  $\text{Ag}_2$ - $\text{O}_4$ ,  $\text{Ag}_2$ - $\text{O}_7$ , and  $\text{Ag}_2$ -(midpoint of  $\text{C}_4$ - $\text{C}_5$ ) are the shortest distances and are in a roughly tetrahedral configuration (dotted lines).

of the crystal at intervals of  $c/2$ , each ring being rotated  $35.7^\circ$  from its nearest neighbors above and below. Each silver ion interacts with only one double bond, all other double bonds directionally feasible being greater than 5 Å distant. The closest approach of any two silver ions is 4.5 Å. Several nitrate groups surround the silver ions (Figure 1); five oxygen atoms approach within 3 Å, and three of these are close enough to 2.46, the sum of the atomic radii, to suggest some degree of covalency.<sup>8</sup> These three oxygens together with the midpoint of the interacting double bond form a roughly tetrahedral arrangement around silver.

The average N-O bond length of 1.25 Å compares well with values determined in other silver nitrate complexes<sup>8,10</sup> and in  $\text{AgNO}_3$  itself.<sup>20</sup> It is slightly greater than the value of  $1.218 \pm 0.004$  Å reported<sup>21</sup> for  $\text{NaNO}_3$ . The average O-N-O bond angle is  $120^\circ$ , and the group is planar within experimental error.

The local environment of the nitrate group consists of three silver ions ( $\text{Ag}_2$ ,  $\text{Ag}_4$ , and  $\text{Ag}_5$ ) within 3.25 Å of the nitrogen atom which describe a plane somewhat above and parallel to the  $\text{NO}_3$  plane.  $\text{Ag}_3$  lies below and at a distance of 4.25 Å from the nitrogen atom. As is indicated by the Ag-O bond lengths in Table III, the silver-oxygen coordination is not simple. It appears as if each silver ion above the  $\text{NO}_3$  group interacts with two oxygens and that  $\text{Ag}_3$  is coordinated only to  $\text{O}_3$ .

Silver anisotropic temperature parameters,  $U_{ij}$ 's, are given in Table IV. Also tabulated are the direction cosines ( $\phi$ ,  $\psi$ , and  $\omega$  corresponding to the cell edges  $a_1$ ,  $a_2$ , and  $c$ , respectively) and root-mean-square displacements of the principal axes of the ellipsoid of vibration. The errors in the directions of the principal axes are large. The only general conclusion drawn is that the most extensive thermal vibration is approximately along the  $c$  axis but is tilted slightly so that principal axis  $P$

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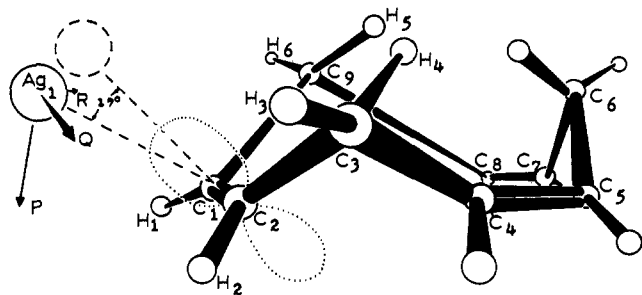


Figure 2. The cyclononatriene ring with assumed hydrogen positions. The silver ion is shown interacting with carbons  $C_1$  and  $C_2$  and distorted  $17^\circ$  from the normal position (dotted lines) along the perpendicular bisector of the ethylene group.  $P$ ,  $Q$ , and  $R$  are the principal axes of thermal motion for the silver ion. One  $\pi$ -bonded  $p$  orbital is shown in its normal position. The lower lobe is convergent with five other lobes below the ring.

(Figure 2) lies almost parallel to the plane  $C_9-C_1-C_2-C_3$ . Therefore the silver motion is perpendicular to the direction of the  $p$  orbitals and allows the silver to remain approximately equidistant from the double bond throughout the vibration.

Table IV. Anisotropic Thermal Motion Parameters<sup>a</sup>

Values of $U_{ij}$ for Silver					
$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{23}$	$U_{13}$
0.01898 (0.00075)	0.01829 (0.00073)	0.03493 (0.00046)	0.00968 (0.00072)	0.00066 (0.00051)	0.00299 (0.00051)
Direction Cosines and Root-Mean-Square Values of Principal Axes					
Axis	$\phi$	$\psi$	$\omega$	$\sqrt{\mu^2}$ (Å)	
$P$	-0.84	0.87	0.17	0.1283 (31)	
$Q$	-0.50	-0.49	0.17	0.1365 (29)	
$R$	0.24	-0.07	0.97	0.1904 (14)	

<sup>a</sup> Anisotropic temperature factors were calculated and refined in the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$  and were converted [D. W. J. Cruickshank, *Acta Cryst.*, **19**, 153 (1965)] to  $U_{ij}$ 's according to  $U_{11} = \beta_{11}/a^2 \cdot 2\pi^2$ , etc.

## Discussion

The carbon ring geometry is almost identical with that of the uncomplexed *cis,cis,cis*-1,4,7-cyclononatriene.<sup>6</sup> The only possibly significant change is a stretching of the  $C_1-C_2$  bond from 1.34 to 1.38 Å which would indicate a weakening due to the silver interaction as is also indicated by infrared studies of other silver  $\pi$  complexes.<sup>22</sup> The increase in the normal trigonal angles to an average of  $124^\circ$  has the effect of separating the intraannular hydrogen atoms as discussed previously.<sup>6</sup> It would appear, therefore, that the structure of the cyclic olefin is changed little, if at all, with silver complex formation.

At the request of a referee, an attempt was made to observe the effect of the hydrogen atoms on the ring geometry. The hydrogen positions (Table V) were not apparent in the difference Fourier maps and were therefore estimated using standard criteria. Two cycles of least-squares refinement resulted in a shortening of the  $C_1-C_2$ ,  $C_2-C_3$ , and  $C_3-C_4$  bond lengths to 1.372, 1.514, and 1.536 Å, respectively. The angle  $C_2-C_3-C_4$  is

(22) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, **37**, 249 (1964).

increased to  $109.4^\circ$ ,  $C_1-C_2-C_3$  to  $126.9^\circ$ , and  $C_3-C_4-C_5$  to  $123.8^\circ$ . These values generally show poorer agreement with normal bond lengths and angles than those previously obtained (Table III). Also, with the exception of the angle  $C_2-C_3-C_4$ , all shifts were within one standard deviation. Therefore the shifts were considered meaningless and Tables II-IV, which are based on the final refinement without the hydrogen atoms, were retained.

Table V. Estimated Hydrogen Coordinates

Atom	$x/a_1$	$y/a_2$	$z/c$
H <sub>1</sub>	0.859	0.383	0.434
H <sub>2</sub>	0.741	0.210	0.427
H <sub>3</sub>	0.625	0.141	0.242
H <sub>4</sub>	0.648	0.254	0.182

The Ag-C distances of 2.379 and 2.411 Å are within error of those obtained for the humulene-silver nitrate adduct,<sup>10,11</sup>  $C_{15}H_{24}(AgNO_3)_2$ , and the silver nitrate adduct of norbornadiene,<sup>13</sup>  $C_7H_8(AgNO_3)_2$ . Corresponding values for the silver nitrate adduct of cyclooctatetraene,<sup>8</sup>  $C_8H_8AgNO_3$ , and its dimer,<sup>9</sup>  $C_{16}H_{16}AgNO_3$ , are approximately 0.1 Å longer due to the interaction of two or more ethylenic bonds with each silver ion.

The slight difference in the two Ag-C distances has been observed in all the silver  $\pi$  complexes thus far studied in detail. Turner and Amma<sup>23</sup> have explained the discrepancy for silver aromatic complexes in terms of molecular orbital theory. The 5s orbital of silver is expected to accept electrons from the bonding  $\pi$  orbital ( $e_1$ ) and the filled d orbitals to donate electrons to the antibonding  $\pi$  orbital ( $e_2$ ). The silver ion seeks a position allowing maximum overlap, which is directly above one of the carbon  $p$  lobes for the 5s, but is above and symmetrically between two carbon atoms for the d orbital. It is postulated that the equilibrium is a compromise somewhat off center, hence the difference in bond lengths. The same argument can be applied to Ag-olefin complexes although the observed discrepancy is considerably less than in Ag-aromatic complexes.

Several considerations enter a rationale for the fact that in  $C_9H_{12}(AgNO_3)_3$  the plane  $Ag_1-C_1-C_2$  is not perpendicular to the  $C_1-C_2-C_3-C_9$  plane but rather forms an angle of  $107^\circ$  with it (Figure 2). This distortion of  $17^\circ$  from the normal silver position which would assure maximum overlap with the  $\pi$  orbital can be explained by (a) steric repulsions between the silver ion and the intraannular hydrogens or carbon atoms  $C_3$  and  $C_9$ ; (b) a twisting of the  $\pi$ -bonded  $p$  orbitals themselves so that silver is, in fact, in the optimum position for overlap; or (c) homoconjugation.

That steric effects play an important role in forcing the silver ion away from the ring is unlikely since in the normal position silver is encircled by a nearly symmetrical ring of hydrogen atoms (Table VI). Carbon atoms  $C_9$  and  $C_3$  would be too far away (3.3 Å) and in unfavorable directions to exert much steric influence. Also there is no evidence of twisting of the

(23) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).

Table VI. Estimated Hydrogen to Silver Distances (A)

Ag <sub>1</sub> -H <sub>1</sub>	2.53	Ag <sub>n</sub> -H <sub>1</sub> <sup>a</sup>	2.78
Ag <sub>1</sub> -H <sub>2</sub>	2.54	Ag <sub>n</sub> -H <sub>2</sub>	2.78
Ag <sub>1</sub> -H <sub>3</sub>	3.49	Ag <sub>n</sub> -H <sub>3</sub>	3.26
Ag <sub>1</sub> -H <sub>4</sub>	3.49	Ag <sub>n</sub> -H <sub>4</sub>	3.04
Ag <sub>1</sub> -H <sub>5</sub>	3.40	Ag <sub>n</sub> -H <sub>5</sub>	2.94
Ag <sub>1</sub> -H <sub>6</sub>	3.40	Ag <sub>n</sub> -H <sub>6</sub>	3.15

<sup>a</sup> Ag<sub>n</sub> refers to silver in the normal position estimated at  $x/a_1 = 0.850$ ,  $y/a_2 = 0.289$ ,  $z/c = 0.187$ .

C<sub>3</sub> and C<sub>9</sub> atoms about the C<sub>1</sub>-C<sub>2</sub> bond. The dihedral angle between C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub> and C<sub>2</sub>-C<sub>1</sub>-C<sub>9</sub> is  $1.8 \pm 2.3^\circ$ .

That the divergent lobes of the p orbitals are twisted outward from their normal positions (assuming sp<sup>2</sup> hybridization) is consistent with the argument<sup>24</sup> that in *cis*-ethylenic systems the  $\pi$ -bonded carbon p orbitals are distorted in order to relieve strain due to bond oppositions. (It is noteworthy that for the *trans* double bond in the humulene-silver nitrate adduct the silver ion is distorted only 5° from the normal position, whereas for the *cis* double bonds in the norbornadiene adduct, the distortion is approximately 24°.)

Finally, a distortion of the p orbitals could be attributed to a rotation of the p orbitals about the C<sub>1</sub>-C<sub>2</sub>

(24) P. D. Gardner, R. L. Brandon, and N. J. Nix, *Chem. Ind. (London)*, 1363 (1958).

axis affecting a further spreading of the divergent lobes and a congestion of those which are convergent. The driving force for such a distortion would be a stabilization due to increased overlap of the convergent lobes and resulting homoconjugation. It is unlikely that homoconjugation is a very important factor in the bonding of the complex. Homoaromaticity in cyclonatriene itself is expected to be small according to simple LCAO-MO calculations,<sup>3,4</sup> and it would seem reasonable that the silver ion would tend to withdraw electrons during complex formation, thus further decreasing any existing p-orbital overlap. Also, increases in the trigonal carbon angles and a decrease in the tetrahedral angles of the ring, which would be expected to accompany significant homoconjugation, are small and can be explained by the intraannular hydrogen interactions.

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## Proton and Phosphorus-31 Nuclear Magnetic Resonance Studies of Tetraalkoxyphosphonium Hexachloroantimonates and Related Compounds<sup>1a</sup>

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Contribution from the Department of Isotope Research, Weizmann Institute of Science, Rehovoth, Israel. Received November 15, 1966

**Abstract:** Tetramethoxyphosphonium hexachloroantimonate (Ia) was obtained in moderate yield from the reaction between trimethyl phosphite and methyl hypochlorite in the presence of antimony pentachloride (reaction ii, X = O). Proton and phosphorus-31 nuclear magnetic resonance (nmr) and infrared and conductivity studies support this formulation. Evidence was also obtained for the formation of the triethoxymethoxy- and triphenoxy-methoxyphosphonium cations. These results confirm that such salts are intermediates in the reaction between phosphite triesters and alkyl hypochlorites. The control reaction (iii) between trimethyl phosphite and antimony pentachloride gave a minor product which was shown to be trimethoxymethylphosphonium hexachloroantimonate (II), the intermediate from intermolecular transmethylation.

Current advances in the understanding of the mechanisms of phosphorus reactions owe much to the detection and characterization of four- and five-covalent intermediates resulting from valency expansion of phosphorus(III) compounds.<sup>2-11</sup> While stable pentaalkoxy-

phosphoranes<sup>2</sup> and trialkoxyalkylphosphonium salts<sup>3,4</sup> have been isolated, the tetraalkoxyphosphonium salts have only been tentatively identified as transient intermediates. Denney and Relles<sup>12</sup> observed their formation using proton nmr in the reactions between trialkyl phosphites and neopentyl hypochlorite (reaction i).

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