The Crystal and Molecular Structure of the Silver Nitrate Complex of *cis,cis,cis*-1,4,7-Cyclononatriene, $C_{9}H_{12}(AgNO_{3})_{3}$

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Abstract: The structure of the silver nitrate π complex of cis, cis, cis, cis, 1,4,7-cyclononatriene, C₂H₁₂(AgNO₃)₃, has been determined by a three-dimensional single-crystal X-ray diffraction investigation. The complex crystallizes in space group R3c; cell dimensions for the triply primitive hexagonal cell are a = 16.258 and c = 9.556 A at approximately -125° . 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 π -bonded p orbitals. The silver ions are distorted 17° in the direction of the *cis* hydrogens.

The structure of cis, cis, cis-1, 4, 7-cyclononatriene, C_9H_{12} ,²⁻⁴ is known to have a crown configuration.5,6 Silver complexes of olefins are well known7 and several⁸⁻¹³ 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 C₃H₁₂(AgNO₃)₃ were prepared¹⁴ 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 *hh*0l, required the space group to be R3c or $R\bar{3}c$. Cell dimensions obtained from film measurements and an approximate density (by flotation) of 2.9 g/cm³ 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 R3c, since R3c would have required the molecule to have 3-C_{3i} or 32-D₃ symmetry.

Two sets of three-dimensional, low-temperature intensity data were collected: initially (a) integrated Weissenberg multiple film data, using Cu Ka radiation, of levels hki0-hki3 and 0kil-8kil, and for later refinement (b) counter-diffractometer data, collected manually with Mo K α 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

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with diffractometer 2θ data, were $a = 16.258 \pm 0.005$ and c = 9.556 ± 0.003 A at approximately -125° .

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 $0.05I_{\rm obsd}$ to avoid accidental agreement. Standard errors for the counter data were based on counting statistics as described by Johnson.¹⁶ Cell dimensions and errors were determined using the least-squares program by Heaton, Gvildys, and Mueller.¹⁶ Patterson and electron-density maps were computed using the Gvildys Fourier summation program.17 The Busing and Levy full-matrix leastsquares program¹⁸ was used for the structure refinement, and their function and error program¹⁹ was used for calculation of bond distances, angles, anisotropic parameters, and their respective standard deviations.

Structure Determination. The structure was solved by the heavyatom 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 leastsquares refinement. Two cycles, varying the silver coordinates and the absolute scale factor, decreased the residual, $R = \Sigma ||F_{\circ}|$ - $|F_c| |/\Sigma |F_o|$, 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 $I_{\text{scaled}} = k_i I_{\text{obsd}} \exp(-B_i)$ $\sin^2 \theta / \lambda^2$), 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^a

Table I. Observed and Calculat			
hk0	3 4 2751 2778 1539 2313	3 5 1721 1777 1063 -1424	5 11 #406 502 -450 -222
	6 4 2210 2234 1362 1771	6 5 1317 1357 1332 258	0 12 1467 1497 863 -1223
	9 4 2622 2620 -2506 764	9 5 1465 1513 268 1489	3 12 882 820 354 739
3 0 2949 2901 859 2771	12 4 675 598 -594 74	12 5 1043 1046 -850 610	1 13 672 789 368 +698
6 0 5646 5761 -2983 4928	1 5 +233 389 -170 350	1 6 2022 2120 -595 2035	
9 0 3080 3008 -1191 -2762	4 5 651 598 593 -81	4 6 1524 1550 -872 1282	<u>hk7</u>
12 0 2083 2107 -1325 -1638	7 5 907 902 873 227	7 6 2602 2679 -1968 -1817	
15 0 1469 1464 1394 448	10 5 1412 1400 117 1396	10 6 704 676 252 -627	2 1 1889 2005 -959 -1761
1 1 2425 2469 -2469 C	13 5 #427 509 -479 -173	2 7 2151 2204 -507 -2145	5 1 988 1064 1061 -76
4 1 2247 2193 1061 *1919	2 6 1846 1808 975 -1523	5 7 #358 148 147 14	8 1 1664 1716 1714 70
7 1 771 864 633 588	5 6 1662 1701 -1592 600	8 7 1087 1125 1035 440	11 1 1197 1200 61 1199
10 1 1635 1663 36 1662	8 6 #367 240 123 -206	0 8 937 908 707 569	3 2 1260 1313 1242 427
13 1 1538 1569 -800 -1350	11 6 1233 1311 366 -1259	3 8 970 1002 -114 996	6 2 1172 1162 -1091 401
16 1 +430 407 -84 -398	0 7 4416 4434 -4299 1084	6 8 871 876 +672 -563	9 2 #379 511 -247 447
2 2 667 545 -545 0	3 7 975 1016 -433 -920	9 8 #417 169 166 31	12 2 1074 1041 90 -1037
5 2 3053 2953 -220 -2945	6 7 2885 2961 1002 -2786	1 9 737 677 650 +188	1 3 1839 1829 -1629 831
8 2 1367 1330 955 -926	9 7 1107 1170 586 1012	4 9 1580 1646 1610 -341	4 3 1221 1215 -1207 -136
11 2 1511 1534 1506 293	1 8 2597 2575 2560 275	7 9 1144 1123 -389 1054	7 3 981 1059 880 -588
14 2 657 753 -A8 748	4 8 1072 1088 -204 1069	2 10 1288 1355 -1040 -869	10 3 +414 138 -74 117
3 3 2815 2703 -2703 0	7 8 1129 1146 -948 644	5 10 799 795 463 646	2 4 1228 1242 -93 1239
6 3 2928 2917 2859 580	10 8 727 774 -333 -698	8 10 841 817 341 -743	5 4 1456 1502 -247 1481
9 3 600 656 -461 -468 12 3 1648 1611 14 1611	2 9 *309 439 -324 -297 5 9 1232 1175 -240 1151	0 11 2162 2236 -1262 1846 3 11 1487 1468 -1237 -790	8 4 1391 1409 -945 -1044 3 5 2059 2106 273 -2088 6 5 934 883 597 650
15 3 #406 534 427 -320	8 9 *390 61 13 59	6 11 1373 1438 -519 -1341	9 5 1373 1352 815 1079
4 4 #242 343 -343 0	0 10 2266 2245 -1806 1333	1 12 874 904 894 -136	
7 4 2530 2586 -1664 1980 10 4 521 557 -327 -451	3 10 1242 1210 874 -836 6 10 1349 1268 -631 -1100 9 10 1098 1070 702 808	4 12 #412 461 452 -88 2 13 1323 1365 -360 1317	1 6 #361 113 -91 -68 4 6 1164 1132 1087 -316 7 6 #393 248 217 -119
13 4 1251 1276 -464 -1189 5 5 1681 1407 -1607 P 8 5 683 707 -455 -541	1 11 971 914 -619 -672	0 14 1324 1360 1322 -320 1 15 991 909 -878 -235	2 7 847 846 -625 570 5 7 595 623 -433 -448
11 5 699 657 385 -533	4 11 588 604 -131 -590 7 11 868 880 632 -613 2 12 636 413 -394 -470	<u>hk5</u>	8 7 878 817 -543 -611 3 8 1208 1249 -1100 -590
9 6 2393 2429 -1548 1877	5 12 1469 1441 1395 361	3 1 2097 2120 2098 306	6 6 713 656 368 529
	0 13 3480 3509 1752 3040	6 1 #298 487 -127 470	1 9 806 851 212 825
7 7 1828 1891 1891 0	3 13 1123 1110 -908 638	9 1 1671 1686 723 1524	4 9 +412 410 -240 -333
	1 14 #387 385 -266 -279	12 1 #381 183 -179 40	2 10 1472 1491 1253 -809
Q0 7 1716 1708 1700 167 8 8 1447 1391 -1391 1 91 8 1038 1047 -117 +1040	4 14 981 972' 917 322	1 2 3157 3120 -207 -3113	3 11 1481 1484 -1274 760
	2 15 #427 437 182 -397	4 2 1292 1311 325 1270	1 12 +425 80 58 -55
9 9 #412 236 -236 P	0 16 892 831 798 -231	7 2 1546 1571 1189 1028 10 2 1906 1929 -1928 64	<u>hk8</u>
<u>hk1</u>	<u>hk3</u>	13 2 #419 154 57 +143 2 3 3048 3045 -2454 1803	2 0 1576 1605 -1042 -1220
2 1 3888 3850 1701 3454	1 1 3468 3466 3308 1034	5 3 2603 2581 -1851 -1798	5 n 725 729 -153 713
5 1 1368 1366 -1390 417	4 1 5050 5042 -1587 4786	8 3 1302 1303 1032 -795	A 0 #376 463 240 -396
8 1 2194 2281 -2275 162	7 1 1314 1241 -765 977	11 3 1550 1582 1557 284	11 0 1038 1083 -729 -802
11 1 1821 1816 768 -1644	10 1 2253 2255 -1863 -1271	3 4 1171 1094 795 -751	0 1 1615 1693 -131 1686
14 1 1572 1569 890 -1292 3 2 4614 4519 -4301 -1389	13 1 #374 163 -151 -62	A 4 868 842 -617 573	3 1 613 677 -328 592
	2 2 1485 1557 1259 -917	9 4 #401 469 144 -447	6 1 1409 1281 -1058 -722
6 2 1484 1506 1505 -27	5 2 2168 2277 985 -2053	12 4 1364 1360 -257 -1335	9 1 625 576 512 -263
9 2 652 631 282 -565	8 2 2699 2749 -344 2727	1 5 1698 1720 -1712 -159	1 2 1174 1120 760 -822
12 2 1981 1959 -1012 1677	12 2 *404 1735 758 *1561	4 5 1408 1335 891 994	4 2 1381 1355 1326 -263
15 2 719 626 140 -610	14 2 1430 1395 -1049 -921	7 5 840 753 567 -495	7 2 1537 1505 148 1496
1 3 2905 2855 2797 570 4 3 2159 2099 1813 1057	3 3 2583 2534 -2459 613 A 3 729 790 357 -705	10 5 1394 1488 -926 1166 2 6 1531 1487 1392 -524	10 2 825 828 -369 74 2 3 #379 253 -27 -252 5 3 1086 1095 882 650
7 3 1384 1376 -977 971 10 3 #355 230 226 -44	9 3 1960 1873 1497 -1124 12 3 1723 1726 1378 1040 1 4 483 4458 -2554 -3654	5 6 1251 1191 154 1181 8 6 879 890 -538 749 11 6 1084 1087 -886 -630	5 3 1086 1095 882 650 8 3 794 798 -274 -750 0 4 690 1229 -428 1152
13 3 +384 202 202 -4 2 4 3155 3062 947 -2912	4 4 1593 1652 1543 -590	3 7 1544 1571 -1040 -1177	3 4 1185 1215 -1052 -607 6 4 1059 1073 -962 -475
5 4 2714 2658 1546 -2162 8 4 2995 3002 1505 2598 11 4 934 931 -555 748	10 4 1987 1956 -1598 1126	6 7 *395 272 10 -272 9 7 858 881 528 -705 1 8 2185 2136 -2097 409	9 4 1043 1011 751 -677 1 5 636 621 204 -566
14 4 1422 1399 -1398 -68	1 13 4 #419 195 -183 -69 2 5 2098 2097 1182 1732 5 5 3341 3380 -3361 352	4 8 2392 2427 730 -2314 7 8 910 878 359 -801	4 5 + 373 269 191 145 7 5 + 414 105 -75 74
3 5 4493 4529 -2457 3805 6 5 1184 1159 -587 -999 9 5 2245 2277 -1384 -1824	8 5 # 361 341 -47 338 11 5 1545 1560 393 =1509	2 9 738 707 582 401 5 9 2129 2148 -808 1991	2 6 883 823 -262 780 5 6 704 703 591 -382
12 5 1729 1732 1729 -104	3 6 992 1055 442 958	A 9 887 960 -775 -567	0 7 2111 2050 1952 -625
1 6 854 714 -693 -174	6 6 #346 448 -440 -81	3 10 +404 217 193 98	3 7 705 729 386 614
4 6 2043 1977 -1558 -1216	9 6 1210 1274 -1187 -464	6 10 796 852 470 711	6 7 1419 1375 -380 1321
7 6 9346 370 -8 -370	12 6 680 712 189 -686	1 11 1199 1179 617 1005	1 8 1393 1363 -1363 34
1 0 6 722 787 257 -744	1 7 1552 1555 -1055 -1142	4 11 647 611 -487 -369	4 8 725 780 246 -740
2 7 2172 2155 1636 -1403	4 7 2166 2148 2072 -566	2 12 1176 1156 -745 -864	2 9 +412 91 -47 7#
5 7 893 935 756 550	7 7 * 3 84 492 488 -59	1 14 946 946 550 770	0 10 682 600 447 -405
8 7 843 864 346 785	10 7 756 701 -284 640		3 10 687 656 -491 435
1 1 7 795 762 -743 -171 3 8 2262 2264 1401 1778	2 8 2648 2753 -1139 -2506 5 8 #361 69 25 -65	<u>hk6</u>	1 11 * 430 267 250 ¥ 3
6 8 #361 543 -512 -181	8 8 1719 1697 1697 -21	0 0 4572 4666 -4347 1695	<u>hk9</u>
9 8 947 902 -284 856	3 9 1579 1629 1409 81P	3 0 1277 1280 134 -1273	
1 9 2599 2575 -124 -2572	6 9 1148 1241 -1214 256	6 0 3154 3098 723 -3013	1 1 1595 1607 -1413 745
4 9 #352 401 396 -65	9 9 781 639 -603 -213	9 0 1938 1819 1312 1259	4 1 1597 1588 14 -1568
7 9 1004 1030 981 315	1 10 2206 2218 -1165 1887	12 0 1340 1399 1048 927	7 1 576 531 315 +427
10 9 1123 1066 -996 -382	4 10 1345 1328 -1192 -585	1 1 1075 1020 1001 -199	2 2 569 490 -479 1 ^A 3
2 10 2402 2460 -2263 964 5 10 2047 2064 -1491 -1425	7 10 698 789 -155 -773 2 11 #384 76 51 .57	4 1 1954 1953 -1417 1344 7 1 513 504 -390 -316	5 2 1068 1068 -328 1017 8 2 947 950 54 ~949 3 3 533 604 602 44
A 10 1720 1754 652 -1628	5 11 1914 1947 557 1866	10 1 1438 1463 -160 -1454	6 3 835 775 296 71e
3 11 2133 2111 2107 -134	3 12 1566 1587 824 -1356	13 1 1061 1018 777 657	
6 11 1200 1196 -661 997 1 12 #379 297 -232 -185	6 12 + 430 402 200 349 1 13 + 376 284 190 211	2 2 + 291 431 - 303 - 307 5 2 1628 1753 625 1638	1 4 1532 1551 855 1295 4 4 740 721 -676 250 7 4 773 725 -719 92
4 12 1419 1408 238 1387 7 12 #404 234 178 -154 2 13 #376 115 115 13	4 13 #419 202 193 -56 2 14 1595 1540 -1032 1143	8 2 557 536 -165 510 11 2 1312 1283 -1248 -300 0 3 1996 1961 1265 1499	2 5 1011 993 -694 -710
5 13 #409 204 -203 -25	<u>hk4</u>	3 3 1307 1344 1334 -170	5 5 1387 1548 1477 -484 3 6 634 604 -454 -397 1 7 \$393 423 375 195
3 14 1046 1187 -295 -1145	1 0 2180 2265 62 -2264	9 3 #406 465 130 447	4 7 759 719 -719 1/
1 15 1629 1627 -1570 427	4 0 3664 3720 -2651 -2609		2 8 924 893 407 655
hk2	4 0 3664 3720 -2651 -2609 7 0 4115 4143 4037 -930 10 0 2029 2074 2074 2	12 3 856 779 -332 -705 1 4 1879 1914 -1556 -1115 4 4 *342 97 72 65	<u>hk10</u>
2 0 5172 5365 4028 3543	13 0 2353 2390 -1129 2106	7 4 1497 1460 891 -1156	1 0 881 1029 28 1079
5 0 2728 2668 1329 -2314	2 1 2110 2122 1998 715	10 4 630 720 385 608	
R D 627 499 -495 5H	5 1 947 970 -341 904	2 5 1757 1794 265 -1774	4 n 1089 1045 1000 302
11 0 1398 1440 1016 1022	8 1 1896 1931 -1775 761	5 5 1603 1597 1592 -128	7 0 1287 1244 -1152 464
1 0 1442 1416 -1384 -299	11 1 627 890 151 -877	8 5 + 379 332 84 321	2 1 853 842 -836 100
0 1 3279 3170 1456 -2816	14 1 * 414 392 299 -253	11 5 575 4A2 -409 256	5 1 #417 185 -146 -114
3 1 1494 1261 -959 -849	0 2 3654 3614 -590 3564	n 6 3302 3356 2319 2427	0 2 949 897 174 -880
6 1 2833 2826 985 2649	3 2 1163 1167 -928 709	3 6 1753 1780 -1614 752	3 2 #409 554 408 -375
9 1 809 840 -837 71	6 2 1320 1270 -1034 -738	6 6 1622 1579 -1566 206	6 2 # 427 453 277 359
12 1 1389 1346 -1308 -317	9 2 *352 327 100 -311	9 6 1172 1137 419 -1057	1 3 # 393 255 247 -A1
15 1 164 1156 941 -672 1 2 2274 2264 -1972 1111	12 2 * 379 489 279 -402	1 7 #352 418 -140 394	4 3 867 848 321 -785
	1 3 1431 1463 -670 -1300	4 7 1716 1689 1465 841	2 4 719 696 -638 238
4 2 3706 3702 -3702 -33	4 3 1788 1752 -1127 1342	7 7 1007 1008 -902 450	5 4 + 404 202 - 65 191
7 2 2959 2985 1068 -2787	7 3 1179 1162 469 -1063	2 8 677 616 -578 -213	0 5 + 412 863 845 173
10 2 1986 1999 1541 -1273	10 3 1368 1358 -1265 -492	5 8 571 562 -6 -562	3 5 756 810 -214 7×1
13 2 1346 1347 969 936	13 3 694 811 798 144	8 8 696 744 729 -147	1 6 1038 1020 20 -1020
2 3 841 857 826 -227	2 4 2207 2278 2197 -602	0 9 1833 1786 228 -1771	<u>hk11</u>
5 3 2152 2208 -1300 -1785	5 4 721 657 398 523	3 9 826 904 138 +894	
8 3 1235 1226 -173 1213	8 4 1614 1607 689 1452	6 9 1193 1192 1068 531	3 1 823 801 - 494 344
11 3 1161 1149 758 -863	11 4 * 384 155 -47 -147	1 10 1192 1202 -155 1192	1 2 845 713 97 7#3
14 3 #419 439 -286 333 0 4 2673 2559 922 -2388	0 5 1643 1621 -1022 -1258	4 10 737 732 282 -676 2 11 1443 1457 -1238 767	1 2 845 713 97 727
a The E is more sharing if from		$ = e^{\frac{1}{2}} + 10E + 10E + 10A$ and	10. R. Unchasmid reflections are

^a 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	<i>B</i> , A ²
Ag	0.8717(1) ^a	0.2823(1)	0.2441^{b}	1.09(29)
$\begin{array}{c} C_1 \\ C_2 \end{array}$	0.7969(10)	0.3549(11)	0.3657(14)	1.08(28)
	0.7306(11)	0.2589(11)	0.3624(12)	1.34(27)
C₃	0.6398(12)	0.2111(12)	0.2741 (14)	0.87(29)
O₁	0.2868(7)	0.3018(8)	0.1806 (10)	2.03(22)
O_2	0.2928(7)	0.1792(7)	0.2521 (12)	1.46 (23)
O3	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)

^a Standard deviations are $\times 10^4$ for coordinates and $\times 10^2$ for B's. ^b 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. ^c See Table IV for the anisotropic thermal parameters for silver.

Table III.	Distances	and	Angles	for
C ₉ H ₁₂ (AgN	O ₃) ₃			

Jar 112(1 181 1	0 3/3		
	Bonded Distance	es (A) and Ang	les
$C_2 - C_3$	1.532 ± 0.020	$C_2 - C_3 - C_4$	$107.6 \pm 1.1^{\circ}$
C3-C4	1.542 ± 0.019	$C_1 - C_2 - C_3$	$126.4 \pm 1.2^{\circ}$
$C_1 - C_2$	1.384 ± 0.020	$C_{3}-C_{4}-C_{5}$	$122.9 \pm 1.4^{\circ}$
Ag_1-C_1	2.379 ± 0.015	$Ag_1-C_1-C_2$	$74.5 \pm 0.9^{\circ}$
Ag_1-C_2	2.411 ± 0.014	$Ag_1-C_2-C_1$	$71.9\pm0.9^{\circ}$
$N-O_1$	1.259 ± 0.015	$O_1 - N - O_2$	$117.7 \pm 1.1^{\circ}$
$N-O_2$	1.259 ± 0.014	$O_2 - N - O_3$	$121.9 \pm 1.3^{\circ}$
N-O₃	1.225 ± 0.013	O1-N-O3	$120.4 \pm 1.2^{\circ}$
	Midpoint of C ₁ -C ₂	to Ag ₁ 2.300 =	± 0.014
	Nonbondeo	d Distances (A)
$C_2 - C_4$	2.480 ± 0.020	$O_1 - O_2$	2.155 ± 0.016
C_3-C_9	3.133 ± 0.027	$O_1 - O_3$	2.156 ± 0.015
Ag ₁ –C ₃	3.357 ± 0.016	$O_2 - O_3$	2.172 ± 0.016
Ag_1-C_9	3.281 ± 0.017		
Di	stances (A) and Ang	les in Silver E	nvironment
$Ag_2 - O_2$		$Ag_2 - O_9$	3.190 ± 0.011
$Ag_2 - O_3$	2.927 ± 0.011	$Ag_2 - O_{12}$	3.240 ± 0.011
$Ag_2 - O_4$	2.484 ± 0.010	$O_2 - Ag_2 - O_4$	$97.7 \pm 0.4^{\circ}$
Ag_2-O_5	2.771 ± 0.012	$O_2 - Ag_2 - O_7$	$111.5 \pm 0.3^{\circ}$
$Ag_2 - O_7$	2.474 ± 0.010	$O_4 - Ag_2 - O_7$	$86.3 \pm 0.2^{\circ}$
	(Midpoint of C ₄ -C ₅)	-Ag ₂ -O ₇ 109.9	$0 \pm 0.2^{\circ}$
	(Midpoint of $C_4 - C_5$)		
	(Midpoint of C_4-C_5)	Ag ₂ O ₄ 140.1	$\pm 0.2^{\circ}$
	Distances (A) in 1	Nitrate Enviro	nment
$Ag_2 - O_2$	2.430 ± 0.012	Ag ₄ -O ₁	2.474 ± 0.010
$Ag_2 - O_3$	2.927 ± 0.011	Ag ₄ -O ₃	3.190 ± 0.011
Ag ₃ –O ₃	3.240 ± 0.011	Ag ₅ -O ₁	2.484 ± 0.009
Ag ₃ -O ₁	4.711 ± 0.010	Ag_5-O_2	2.771 ± 0.012
Dihedra	l Angles between Plar	nes Each Define	ed by Three Atoms
	-C3-C4 and C1-C2-C4		$73.0 \pm 1.7^{\circ}$
Agı	$-C_1-C_2$ and C_1-C_2-C	9 10	$07.8 \pm 1.5^{\circ}$
Agı	-C1-C2 and C1-C2-C		$06.4 \pm 1.5^{\circ}$
	C_2-C_3 and a, b plane		$49.3 \pm 0.4^{\circ}$
	$O_2 - O_3$ and a, b plane		$42.4 \pm 0.8^{\circ}$
Ag	$-Ag_4-Ag_5$ and O_1-O_2	-O ₃	$8.3 \pm 1.0^{\circ}$

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

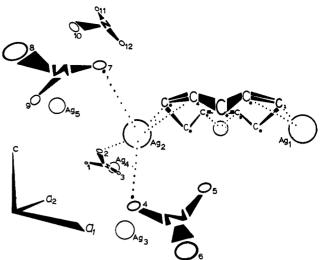


Figure 1. The environment of a silver ion (Ag_2) showing all neighboring oxygen atoms. Ag₁ and Ag₂ are related by a threefold axis; Ag₃, Ag₄, and Ag₅ are related by a 3₁ screw axis. A 3₂ screw axis relates the NO₃ groups 4-5-6, 7-8-9, and 10-11-12. Oxygens O₂, O₃, O₄, O₅, O₇, O₉, and O₁₂ are within 4.0 A of the silver ion. Ag₂-O₂, Ag₂-O₄, Ag₂-O₇, and Ag₂-(midpoint of C₄-C₅) 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° 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 A distant. The closest approach of any two silver ions is 4.5 A. Several nitrate groups surround the silver ions (Figure 1); five oxygen atoms approach within 3 A, and three of these are close enough to 2.46, the sum of the atomic radii, to suggest some degree of covalency.⁸ 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 A compares well with values determined in other silver nitrate complexes^{8.10} and in AgNO₃ itself.²⁰ It is slightly greater than the value of 1.218 ± 0.004 A reported²¹ for NaNO₃. The average O–N–O bond angle is 120°, and the group is planar within experimental error.

The local environment of the nitrate group consists of three silver ions (Ag₂, Ag₄, and Ag₃) within 3.25 A of the nitrogen atom which describe a plane somewhat above and parallel to the NO₃ plane. Ag₃ lies below and at a distance of 4.25 A 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 NO₃ group interacts with two oxygens and that Ag₃ is coordinated only to O₃.

Silver anisotropic temperature parameters, U_{ij} 's, are given in Table IV. Also tabulated are the direction cosines (ϕ , ψ , and ω 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

(20) P. F. Lindley and P. Woodward, J. Chem. Soc., Sect., A, 123 (1966).
(21) R. L. Sass, R. Vidale, and J. Donohue. Acta Cryst. 10, 567.

(21) R. L. Sass, R. Vidale, and J. Donohue, Acta Cryst., 10, 567 (1957).

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° 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 π -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 Parametersª

Values of U_{ii} for Silver					
U_{11}	U_{22}	U_{33}	U ₁₂	U_{23}	U_{13}
0.01898	0.01829) (0.00073)		0.00968 (0.00072)		0.00299 (0.00051)
Direction Cosines and Root-Mean-Square Values of Principal Axes					
Axis	φ	ψ	ω	\mathbf{v}	$\overline{\mu^2}$ (A)
P Q R	-0.84 -0.50 0.24	0.87 -0.49 -0.07	0.17 0.17 0.97	0.1	283 (31) 365 (29) 904 (14)

^a Anisotropic temperature factors were calculated and refined in the form $\exp[-(\beta_{11}h^3 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ and were converted [D. W. J. Cruickshank, *Acta Cryst.*, **19**, 153 (1965)] to U_{ij} 's according to $U_{11} = \beta_{11}/a^* {}^2 2\pi^2$, etc.

Discussion

The carbon ring geometry is almost identical with that of the uncomplexed *cis,cis,cis*-1,4,7-cyclononatriene.⁶ The only possibly significant change is a stretching of the C_1 - C_2 bond from 1.34 to 1.38 A which would indicate a weakening due to the silver interaction as is also indicated by infrared studies of other silver π complexes.²² The increase in the normal trigonal angles to an average of 124° has the effect of separating the intraannular hydrogen atoms as discussed previously.⁶ 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 A, 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° , $C_1-C_2-C_3$ to 126.9° , and $C_3-C_4-C_5$ to 123.8° . 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 ₁	0.859	0.383	0.434
\mathbf{H}_2	0.741	0.210	0.427
\mathbf{H}_{3}	0.625	0.141	0.242
H_4	0.648	0.254	0.182

The Ag–C distances of 2.379 and 2.411 A are within error of those obtained for the humulene–silver nitrate adduct, ^{10,11} C₁₅H₂₄(AgNO₃)₂, and the silver nitrate adduct of norbornadiene, ¹³ C₇H₈(AgNO₃)₂. Corresponding values for the silver nitrate adduct of cyclooctatetraene,⁸ C₈H₈AgNO₃, and its dimer,⁹ C₁₆H₁₆-AgNO₃, are approximately 0.1 A 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 π complexes thus far studied in detail. Turner and Amma²³ 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 π orbital (e_1) and the filled d orbitals to donate electrons to the antibonding π orbital (e₂). 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° with it (Figure 2). This distortion of 17° from the normal silver position which would assure maximum overlap with the π 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 π -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 A) 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 ₁ -H ₁	2.53	Ag _n -H ₁ ^a	2.78	
Ag_1-H_2	2.54	$Ag_n - H_2$	2 .78	
Ag ₁ -H ₃	3.49	Ag_n-H_3	3.26	
Ag ₁ -H ₄	3.49	$Ag_n - H_4$	3.04	
$Ag_1 - H_5$	3.40	$Ag_n - H_5$	2.94	
Ag_1-H_6	3.40	$Ag_n - H_6$	3.15	

^a Ag_n refers to silver in the normal position estimated at $x/a_1 =$ $0.850, y/a_2 = 0.289, z/c = 0.187.$

 C_3 and C_9 atoms about the C_1-C_2 bond. The dihedral angle between C_1 - C_2 - C_3 and C_2 - C_1 - C_9 is $1.8 \pm 2.3^\circ$.

That the divergent lobes of the p orbitals are twisted outward from their normal positions (assuming sp² hybridization) is consistent with the argument²⁴ that in *cis*-ethylenic systems the π -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_1-C_2

(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 cyclononatriene itself is expected to be small according to simple LCAO-MO calculations,^{3,4} 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 Compounds¹⁸

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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 triphenoxymethoxyphosphonium 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.

urrent 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.²⁻¹¹ While stable pentaalkoxy-

phosphoranes² and trialkoxyalkylphosphonium salts^{3,4} have been isolated, the tetraalkoxyphosphonium salts have only been tentatively identified as transient intermediates. Denney and Relles¹² observed their formation using proton nmr in the reactions between trialkyl phosphites and neopentyl hypochlorite (reaction i).

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