the same coordinate axis system as was used for the least-squares planes, with the origin placed on the center of mass. No allowance was made for mixing of libration–vibration motions, since it was felt that this interaction should be small. Examination of the principal diagonal elements of the vibrational tensors of the cation and anion indicates that the principal amplitudes of motion for the anion are larger than those of the cation; this is most likely a result of the cell packing (*i.e.*, the symmetric tetrachloro group "sees" a broader potential well than does the rather asymmetric cation). A comparison of the relative magnitude of the principal librational tensor elements indicates that the more asymmetric cation undergoes a more pronounced anisotropic librational motion than does the anion.

Summary

The heptamethylbenzene–aluminum tetrachloride complex was found to be ionic, with a very nearly symmetric tetrahedral $AlCl_4^-$ group. The cation consists of a seventh methyl group σ-bonded to hexamethylbenzene forming a *gem*-dimethyl group. Two perpendicular planes contain all C atoms of the cation. The ring structure of the cation consists of five sp^2-bonded carbon atoms over which four π electrons are delocalized while the sixth carbon atom possesses somewhat distorted tetrahedral bonding. A simple Hückel MO calculation was performed, and good agreement was obtained between observed and calculated bond distances.

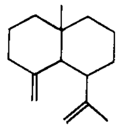
The Crystal Structure of β-Gorgonene–Silver Nitrate[1]

M. Bilayet Hossain and Dick van der Helm[2]

Contribution from the Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069. Received May 27, 1968

Abstract: The crystal structure of β-gorgonene–silver nitrate, $C_{15}H_{24}\cdot AgNO_3$, a metal adduct of a new sesquiterpene, has been determined by heavy-atom technique and refined by three-dimensional least-squares methods. The final *R* index for 1181 reflections (both observed and unobserved) is 0.066, and the standard deviations in the positions of the C, N, and O atoms are in the range of 0.01–0.02 Å. The crystals are orthorhombic, space group $P2_12_12_1$, with a = 9.036 Å, b = 21.786 Å, and c = 8.008 Å, Z = 4. The bond distances and angles are normal. The gorgonene molecule does not follow the familiar "isoprene rule" of head-to-tail arrangement, and the isopropyl residue is found to be arranged differently relative to β-selinene. The structure consists of parallel chains of $AgNO_3$ lying along the *c* axis. The Ag^+ ion is bonded to two neighboring NO_3 groups and two C–C double bonds of a single gorgonene molecule. $Ag^+\cdots C{=}C$ lengths of 2.44 ± 0.01 and 2.47 ± 0.1 Å, and $Ag^+\cdots O$ contacts ranging from 2.38 ± 0.01 to 2.80 ± 0.01 Å are observed.

During the investigation of various terpenoids found in some marine organisms, a new bicyclic sesquiterpene skeleton has been encountered in the hydrocarbon β-gorgonene (I), isolated from *Pseudopterogorgia americana*.[3,4] Nmr spectral properties clearly indicated the substitution pattern of β-selinene (II), but its physical properties were not compatible with that compound. Its extreme resistance to dehydrogenation prevented direct determination of the carbon skeleton by nmr.[4] Separation from other hydrocarbons in the gorgonians was accomplished by silver nitrate–silicic acid chromatography which converted a portion of the β-gorgonene to the crystalline silver nitrate adduct. The present structure investigation was carried out with a twofold purpose—to find the correct structure of the gorgonene molecule, and to add some crystallographic data to the studies of the complexes formed between Ag^+ ion and π-bonding systems in the unsaturated compounds. Such studies of complexes between heavy metal ions and π-bonding systems in conjugated and unsaturated compounds have received considerable experimental and theoretical[5-9] attention in recent years.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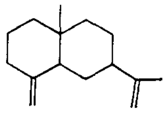
II

Experimental Section

Crystals of β-gorgonene–silver nitrate which were grown from hexane–acetone are silvery needles elongated along the *c* axis. The density was measured by flotation in a mixture of bromobenzene and carbon tetrachloride with some difficulties as the crystals were mildly affected by both liquids. The cell dimensions and space group were obtained from diffraction data collected with the help of a General Electric XRD-5 single crystal diffractometer.

Crystal Data. β-Gorgonene–silver nitrate ($C_{15}H_{24}\cdot AgNO_3$) exhibited the following characteristics: mol wt, 373; mp 132.5–133.5°; orthorhombic; a = 9.037 ± 0.004 Å, b = 21.786 ± 0.007 Å, c = 8.008 ± 0.005 Å; V = 1576.6 $Å^3$; d_m = 1.590 g cm^{-3}, d_c = 1.571 g cm^{-3}, Z = 4; linear absorption coefficient for

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[1] Research supported by the National Institutes of Health, Grant No. GM 11982.

[2] Author to whom inquiries should be made.

[3] L. S. Ciereszko, D. H. Sifford, and A. J. Weinheimer, *Ann. N. Y. Acad. Sci.*, 90, 917 (1960).

[4] P. H. Washecheck, Ph.D. Thesis, University of Oklahoma, Norman, Okla., 1967.

[5] J. Chatt and R. G. Wilkins, *Nature*, **165**, 859 (1950).

[6] J. Chatt and L. M. Vananzi, *ibid.*, **177**, 852 (1956).

[7] R. S. Mulliken, *J. Amer. Chem. Soc.*, 74, 811 (1952).

[8] J. Chatt, *J. Chem. Soc.*, 3340 (1949).

[9] R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951).

Cu Kα radiation = 106.4 cm^{-1}; absent spectra, $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd; space group, $P2_12_12_1$.

Intensity Data. The intensities of all reflections with $2\theta \leq 110°$ (for Cu Kα radiation) were measured on a General Electric XRD-5 diffractometer using a moving-crystal moving-counter technique. Difficulties were encountered due to the slow decomposition of the irradiated crystal. After a few hours exposure in X-rays the crystal turned almost dark brown. There was a steady fall of intensity with exposure time and the rate of decrease in intensities was higher for higher order reflections. With the help of a set of reflections of 2θ values ranging from 16 to 100°, intensities of which were measured every few hours, it was possible to place all the intensities, measured over a period of 2 weeks, on a relative scale. In all, 1181 reflections were recorded by using two crystals (0.10 $\times$ 0.12 $\times$ 0.80 mm and 0.08 $\times$ 0.14 $\times$ 0.74 mm) of which 55 had backgrounds almost as large as their total count. The latter were recorded as "unobserved" reflections with intensity value of one-quarter of the background count.

Absorption and Lorentz polarization corrections were made and a statistical analysis of the intensities gave an over-all isotropic temperature factor, $B = 3.9$ Å^2.

Determination of the Structure. A three-dimensional sharpened Patterson synthesis was carried out by using all the observed data. From the three Harker sections the Ag atom position was found quite easily. Attempts to locate the lighter atoms from the rest of the Patterson peaks were unsuccessful. The superposition method was tried next; as this failed to give any unambiguous result, it was decided to follow the usual heavy-atom technique.

Structure factors for all the reflections were calculated using the positional parameters of silver atom with an isotropic temperature factor of $B = 3.9$ Å^2. The conventional discrepancy factor, R (= $\Sigma|k|F_o| - |F_c||/\Sigma|kF_o|$), was 0.314. A three-dimensional Fourier was calculated using the heavy-atom phases. Reflections with small F_{Ag} were excluded from the Fourier summation.

Although the Fourier map contained several peaks of appreciable heights, it failed to show the NO_3 group or the expected rings of the β-gorgonene molecule. This, however, was not unexpected; the low discrepancy factor already indicated that the silver atom would probably dominate the Fourier. It seemed that a difference Fourier would be less affected by such influence. The silver atom was given anisotropic thermal parameters and these along with the positional parameters were refined by least squares. In two cycles the R was down to 0.286. A difference Fourier was calculated with $(F_o - F_{Ag})$ as the Fourier coefficients. From this difference Fourier map, it was possible to locate the NO_3 group and seven other carbon atoms. The structure factor calculation with these atoms showed an R factor of 0.264. The rest of the structure was obtained in two successive difference Fouriers. The structure factor calculation with all the atoms gave an R of 0.208. In all the calculations, the scattering factors used for Ag$^+$, C, N, and O are those given in the "International Tables for X-Ray Crystallography."[10]

The structure was refined in two stages. In the preliminary stage, the refinements of positional and thermal parameters were carried out by block-diagonal least squares on the IBM 1620 computer. The function minimized was $\Sigma w(F_o - F_c)^2$. Three cycles with isotropic thermal parameters for lighter atoms reduced R from 0.208 to 0.162. Anisotropic temperature factors were introduced for the NO_3 group and seven carbon atoms including those of the isopropenyl group, and in four least-square cycles R was down to 0.114.

At this stage, all the data were corrected for the anomalous dispersion effect of the Ag atom following Patterson.[11] The structure was then refined by least squares using anisotropic temperature factor for all the atoms on IBM 360/40 by using SFLS program by Ahmed.[12] A weighting function of the type $w^{1/2} = 1$ if $F_o \leq P_1$, $w^{1/2} = P_1/|F_o|$ if $|F_o| > P_1$ (= 28.0 e) was used throughout the refinement. In four cycles R was reduced to 0.066. Unobserved reflections were included in the least-squares calculation. The standard deviations of parameters (esd) were estimated from inverse of the last least-squares matrix. The parameter shifts in the last cycle were mostly well below 0.33 esd; the largest was 0.48 esd. A difference Fourier was calculated at this stage. The Fourier contained several peaks of heights acceptable for hydrogen atoms. But as there were too many peaks to choose from, the idea of locating the hydrogen atoms was abandoned.

The final parameters with their standard deviations for all the atoms are listed in Tables I and II; the observed and calculated structure amplitudes (times ten) are on file with the ASIS National Auxiliary Publication Service.[13]

Table I. Final Atomic Coordinates[a]

Atom	x/a	y/b	z/c
Ag$^+$	0.1371 (1)	0.0505 (1)	−0.1802 (1)
O(1)	−0.0280 (13)	0.0134 (6)	−0.4579 (16)
O(2)	0.0951 (15)	−0.0222 (6)	−0.6561 (13)
O(3)	0.2047 (11)	0.0182 (5)	−0.4532 (16)
N	0.0867 (13)	0.0037 (5)	−0.5219 (13)
C(1)	−0.1056 (14)	0.1276 (5)	0.0772 (14)
C(2)	−0.2200 (15)	0.1154 (7)	0.2240 (17)
C(3)	−0.2112 (18)	0.1692 (8)	0.3547 (20)
C(4)	−0.0542 (18)	0.1731 (7)	0.4220 (16)
C(5)	0.0607 (15)	0.1861 (5)	0.2823 (17)
C(6)	0.2158 (17)	0.1817 (6)	0.3660 (19)
C(7)	0.3392 (16)	0.1881 (7)	0.2429 (21)
C(8)	0.3266 (15)	0.1380 (6)	0.1040 (19)
C(9)	0.1737 (13)	0.1434 (5)	0.0249 (16)
C(10)	0.0499 (12)	0.1327 (5)	0.1467 (13)
C(11)	−0.1284 (15)	0.0743 (5)	−0.0458 (15)
C(12)	−0.0732 (16)	0.0176 (6)	−0.0118 (17)
C(13)	−0.2299 (15)	0.0884 (7)	−0.1891 (22)
C(14)	0.0373 (20)	0.2484 (6)	0.2047 (21)
C(15)	0.1519 (19)	0.1626 (6)	−0.1349 (16)

[a] Estimated standard deviations for the last digit are given within parentheses.

Absolute Configuration. The method of Bijvoet, Peerdeman, and van Bommel[14] was used to determine the absolute configuration of the β-gorgonene molecule. The anomalous scattering of Cu Kα X-radiation by Ag is large enough to be generally observable. A series of reflections were chosen the intensities of which were the most sensitive to the anomalous scattering effect. Comparison with the calculated results showed that β-gorgonene has the configuration as shown in Figure 2. Results of the experiment are shown in Table III; observed and calculated values of the quantity $100(|F_+|^2 - |F_-|^2)/(^1/_2)(|F_+|^2 + |F_-|^2)$ are shown for 20 reflections. In this expression $|F_+|$ corresponds to the reflection hkl and its group equivalents ($h\bar{k}\bar{l}$, $\bar{h}k\bar{l}$, $\bar{h}\bar{k}l$) while F_- corresponds to $\bar{h}\bar{k}\bar{l}$ and its equivalents. In all experiments two equivalent reflections of each type were measured. The calculated structure factors in Table III are obtained by using the atomic coordinates as listed in Table II and a right-handed system of axes. The values of $\Delta f'$ and $\Delta f''$ used are those given in the "International Tables for X-Ray Crystallography."[15]

Discussion

Molecular Structure. The bond distances and angles as calculated from parameters of Table I are shown in Figure 1 and Table IV, respectively. Their standard deviations are calculated from uncertainties of the final atomic parameters. The average standard deviation for a C–C bond is 0.02 Å and for C–C–C angle is 1.1°. The rather high standard deviations may be the result of additional uncertainties introduced by various effects, such as thermal libration, random error in data due to crystal decomposition, etc.

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(10) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202–203.

(11) A. L. Patterson, *Acta Cryst.*, **16**, 1255 (1963).

(12) F. R. Ahmed, Division of Pure Physics, National Research Council, Ottawa, Canada, 1966, private communication.

(13) Observed and calculated structure factors have been deposited as Document No. NAPS-00134 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34 St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

(14) J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, **168**, 271 (1951).

(15) Reference 10, p 215.

Table II. Final Anisotropic Temperature Coefficients[a] in the Expression $\mathrm{Exp}[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)]$

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Ag^+	0.0113 (1)	0.00272 (2)	0.0163 (2)	−0.0036 (1)	−0.0007 (3)	0.0012 (1)
O(1)	0.017 (2)	0.0046 (4)	0.027 (2)	−0.005 (2)	0.024 (4)	0.002 (1)
O(2)	0.021 (2)	0.0042 (3)	0.018 (2)	−0.004 (1)	−0.014 (4)	0.005 (1)
O(3)	0.012 (1)	0.0029 (3)	0.030 (2)	−0.005 (1)	0.001 (4)	−0.002 (1)
N	0.014 (2)	0.0024 (3)	0.010 (2)	−0.002 (1)	−0.001 (3)	0.001 (1)
C(1)	0.011 (2)	0.0019 (3)	0.009 (2)	−0.002 (1)	0.002 (3)	0.000 (1)
C(2)	0.009 (2)	0.0030 (4)	0.015 (2)	−0.004 (2)	0.005 (4)	−0.002 (1)
C(3)	0.014 (2)	0.0037 (4)	0.019 (3)	−0.008 (2)	0.011 (5)	−0.003 (2)
C(4)	0.017 (2)	0.0031 (4)	0.011 (2)	−0.004 (2)	0.008 (4)	0.000 (2)
C(5)	0.011 (2)	0.0016 (3)	0.016 (2)	−0.003 (1)	0.001 (4)	0.001 (1)
C(6)	0.014 (2)	0.0022 (3)	0.018 (3)	−0.005 (2)	−0.012 (4)	−0.001 (1)
C(7)	0.011 (2)	0.0032 (4)	0.021 (3)	−0.002 (2)	−0.006 (5)	−0.001 (1)
C(8)	0.012 (2)	0.0023 (3)	0.021 (3)	−0.005 (2)	−0.007 (4)	−0.002 (1)
C(9)	0.009 (2)	0.0017 (3)	0.015 (2)	−0.002 (1)	−0.001 (3)	0.000 (1)
C(10)	0.006 (1)	0.0017 (2)	0.009 (2)	−0.002 (1)	0.003 (3)	−0.001 (1)
C(11)	0.009 (2)	0.0019 (3)	0.012 (2)	−0.001 (1)	0.005 (4)	−0.003 (1)
C(12)	0.013 (2)	0.0021 (3)	0.017 (2)	−0.003 (2)	0.011 (4)	−0.003 (1)
C(13)	0.009 (2)	0.0032 (4)	0.024 (3)	−0.004 (2)	−0.011 (5)	0.001 (1)
C(14)	0.021 (3)	0.0012 (3)	0.025 (3)	−0.003 (2)	0.000 (6)	0.001 (1)
C(15)	0.020 (2)	0.0019 (3)	0.013 (2)	−0.002 (1)	0.001 (4)	−0.003 (2)

[a] Standard deviations for the last digit are given within parentheses.

Table III

h	k	l	Values of $100(\lvert F_+\rvert^2 - \lvert F_-\rvert^2)/{}^1/_2(\lvert F_+\rvert^2 + \lvert F_-\rvert^2)$ Calcd	Obsd
1	1	2	−13.6	−13.0
1	3	1	−16.7	−12.6
3	2	2	+18.2	+12.4
1	2	2	−13.9	−19.3
1	2	5	−35.9	−49.7
1	2	7	+37.2	+21.9
1	4	2	−21.2	−19.4
1	5	1	−21.1	−26.9
1	5	2	+29.4	+30.0
1	5	4	+15.9	+13.2
2	3	2	+15.4	+12.7
3	1	3	−18.8	−25.6
2	4	1	−30.6	−29.1
1	6	1	+53.9	+47.5
1	8	2	+29.2	+20.0
1	9	2	−22.0	−23.9
4	3	4	−33.8	−24.1
4	3	5	+38.8	+28.8
6	4	2	+26.4	+17.7
4	1	2	+20.6	+17.7
1	4	5	−15.6	−21.5

The molecular configuration of β-gorgonene confirms the bicyclic skeleton predicted by nmr studies, but the orientation of isopropenyl group shows that β-gorgonene is a nonfarnesyl, and does not follow the head-to-tail isoprene rule. This poses an interesting question as for the biosynthesis in the formation of β-gorgonene and this problem will be discussed in a separate publication.[16]

The average bond distances of the type sp^3–sp^3, sp^3–sp^2, and sp^2–sp^2 are found to be 1.55 ± 0.02, 1.52 ± 0.02, and 1.36 ± 0.02 Å, respectively. Within experimental error these values are in fair agreement with normal sp^3–sp^3 (1.54 Å[17]), sp^3–sp^2 (1.50 Å[18]), and sp^2–sp^2 (1.34 Å[17]). The bond lengths C_5–C_{10} (1.60 Å) and C_1–C_2 (1.59 Å) are more than 2σ larger than the average. Although larger random errors may cause the variation in bond lengths, the extension of the above-mentioned bonds may be due to the substitution effect on the bond lengths, atoms C_5 and C_1 being fully substituted. Maslen and Oh[19] have discussed the possibility of such bond extension due to the substitution effect. Similar extensions of bond lengths have been observed in the case of methyl melalencate iodoacetate,[20] davallol iodoacetate,[21] and isoeremolactone.[19]

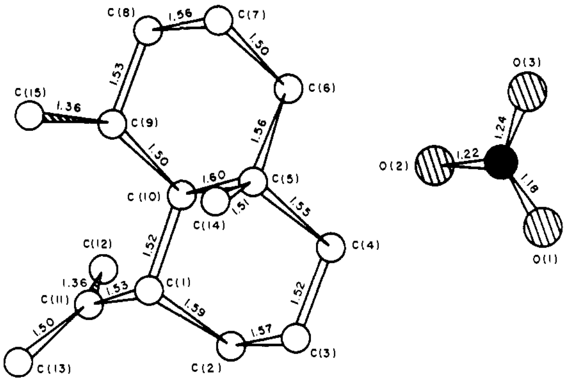

Figure 1. The bond distances in the gorgonene molecule and NO_3 group.

The average value of all the tetrahedral angles in the the gorgonene molecule is 110.2 ± 1.1°. The angles C_9–C_{10}–C_1 (117.6°) and C_{10}–C_1–C_{11} (114.6°) seem to be significantly larger than the average value. The fact that the angle C_2–C_1–C_{11} (105.2°) is also more than 2σ smaller than the average is suggestive that the Ag^+ being bonded in this region of the molecule may have caused a steric strain on the gorgonene molecule. The sums of the angles around two sp^2 atoms C_9 and C_{11} are both 395.6°.

The three NO distances of 1.18, 1.22, and 1.24 are in good agreement with the generally accepted value (1.22

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(16) A. J. Weinheimer, P. H. Washecheck, M. B. Hossain, and D. van der Helm, *Chem. Comm.*, in press.

(17) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958, pp S12–14.

(18) D. R. Lide, *Tetrahedron*, 17, 125 (1962).

(19) E. N. Maslen and Y. L. Oh, Department of Physics, University of Western Australia, Nedlands, private communication.

(20) S. R. Hall and E. N. Maslen, *Acta Cryst.*, **18**, 265 (1965).

(21) Y. L. Oh and E. N. Maslen, *ibid.*, **20**, 852 (1966).

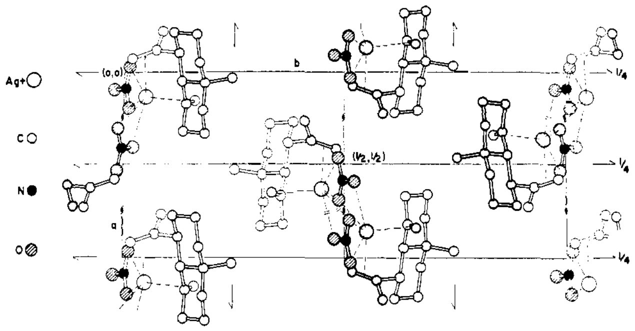

Figure 2. A view of the structure down the *c* axis.

Å) of N–O distances.[22] However, it seems to be an established fact that asymmetry occurs in the NO_3 group bond distances in $AgNO_3$ where one or more oxygen atoms are bonded to Ag atom as demonstrated by the structure work of silver nitrate,[23] silver nitrate–pyrazine complex,[24] and $AgCN{\cdot}2AgNO_3$.[25] In explaining such asymmetry, Britton and Dunitz[25] suggested that there is a correlation between Ag–O distance to corresponding N–O distance such that for shorter Ag–O contact the N–O distance is larger. The N–O distances in the present case are in general agreement with such a hypothesis as shown in comparison in Table V. The sum of the angles at N is 360° which indicates that Ag–O contacts apparently have no effect on the planarity of the NO_3 group.

Table IV. Bond Angles

	θ, deg	$\sigma(\theta)$, deg
C(2)–C(1)–C(10)	110.1	0.9
C(2)–C(1)–C(11)	105.2	1.0
C(10)–C(1)–C(11)	114.6	1.0
C(1)–C(2)–C(3)	109.6	1.1
C(2)–C(3)–C(4)	109.0	1.3
C(3)–C(4)–C(5)	112.3	1.1
C(4)–C(5)–C(10)	108.4	1.0
C(4)–C(5)–C(6)	106.2	1.1
C(4)–C(5)–C(14)	111.6	1.2
C(6)–C(5)–C(10)	107.7	1.0
C(10)–C(5)–C(14)	111.5	1.1
C(5)–C(6)–C(7)	112.4	1.2
C(6)–C(7)–C(8)	110.6	1.2
C(7)–C(8)–C(9)	107.9	1.1
C(8)–C(9)–C(10)	113.2	1.1
C(8)–C(9)–C(15)	123.0	1.2
C(10)–C(9)–C(15)	123.4	1.2
C(1)–C(10)–C(5)	111.2	0.9
C(1)–C(10)–C(9)	117.6	0.9
C(5)–C(10)–C(9)	106.4	0.9
C(1)–C(11)–C(12)	120.6	1.1
C(1)–C(11)–C(13)	114.8	1.1
C(12)–C(11)–C(13)	124.2	1.2
O(1)–N–O(2)	121.5	1.0
O(1)–N–O(3)	121.3	1.0
O(2)–N–O(3)	117.2	1.0

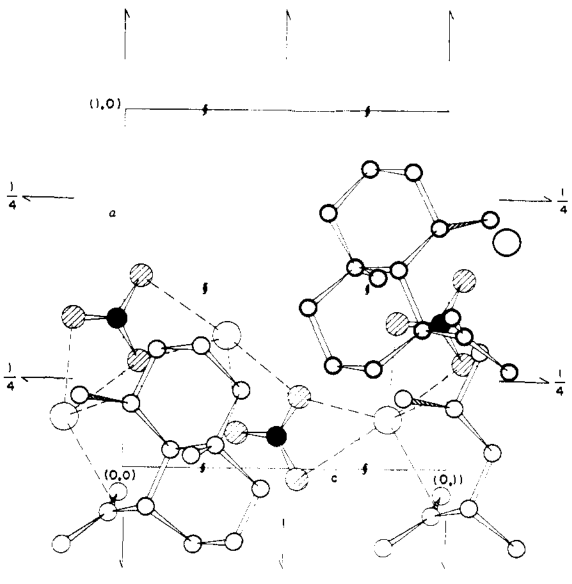

Figure 3. A view of the structure down the *b* axis.

Crystal Structure. The crystal structure of β-gorgonene–silver nitrate is shown in Figures 2 and 3. In Figure 3 only one-half of the total cell contents is drawn. Of special interest in the structure is the role of the Ag^+, which is bonded to two neighboring NO_3 groups and two C–C double bonds of the same gorgonene molecule. Silver nitrate itself forms an endless chain lying parallel to the *c* axis. These chains lie in the (010) and (020) planes. Pairs of gorgonene molecules related by *c*-screw axes at ($^1/_4$, 0, 0) and ($^3/_4$, $^1/_2$, 0) are attached to these chains by $Ag^+\cdots C{=}C$ contacts lying on either side of the mean plane of $AgNO_3$ (Figure 2). All short intermolecular distances of any significance are between the terpene molecule and NO_3 group as shown in Table VI. The lack of close contact between the terpenes themselves indicates a very loose packing of the parallel chains. Such a packing explains the rather thin needle-shaped crystal grown along *c* axis.

Table V

N–O distance, Å	Corresponding Ag–O distance, Å	Ref
1.20	2.70	25
1.27	2.51	
1.31	2.40	
1.19	2.54, 2.51	23
1.23	2.53, 2.73, 2.73	
1.32	2.48, 2.59, 2.99	
1.18	2.80	Present work
1.22	2.50	
1.24	2.38, 2.75	

The surroundings of Ag^+ are shown in Figure 4. The distances and angles indicate a very irregular sixfold coordination. The distances of Ag^+ ion and the midpoint of C_9–C_{15} and C_{11}–C_{12} bonds are 2.46 ± 0.01 and 2.47 ± 0.01 Å, respectively. These values are considerably shorter than 2.57 Å found in $C_6H_6\cdots AgAlCl_4$[26] or in silver cyclooctatetraene nitrate.[27] The asymmetry in nearest metal-carbon distances such as Ag^+–C_9 of 2.63 Å, Ag^+–C_{15} of 2.47 Å and Ag^+–C_{11} of 2.68 Å, Ag^+–C_{12} of 2.44 Å, seems to be a general characteristic of $M^+\cdots C{=}C$ interactions, being true

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Table VI. Intermolecular Distances Less Than 4 Å in ($C_{15}H_{24} \cdot AgNO_3$)

1. (x, y, z)		$C_{10}(1)–O_2(3)$	3.75[a]
2. $(^1/_2 - x, \bar{y}, ^1/_2 + z)$		$C_{10}(1)–N(3)$	3.88
3. $(x, y, z + 1)$		$C_{12}(1)–O_2(3)$	3.34
4. $(x + ^1/_2, ^1/_2 - y, \bar{z})$		$C_8(1)–C_{14}(4)$	3.98
5. $(x - ^1/_2, ^1/_2 - y, 1 - \bar{z})$		$C_3(1)–C_6(5)$	3.99
6. $(-x - ^1/_2, y, ^1/_2 + z)$		$C_2(1)–O_1(6)$	3.90
7. $(^1/_2 - x, y, z - ^1/_2)$		$C_{11}(1)–O_1(6)$	3.71
$C_8(1)–O_1(2)$	3.80[a]	$C_{12}(1)–O_1(6)$	3.69
$C_8(1)–O_2(2)$	3.35	$C_{12}(1)–C_{13}(6)$	3.90
$C_8(1)–O_3(2)$	3.45	$C_{13}(1)–O_1(6)$	3.62
$C_8(1)–N(2)$	3.34	$C_{13}(1)–O_2(6)$	3.61
$C_9(1)–O_2(2)$	3.67	$O_2(1)–O_3(7)$	2.90
$C_9(1)–O_3(2)$	3.69		
$C_9(1)–N(2)$	3.89		
$C_{12}(1)–O_3(2)$	3.45		
$C_{15}(1)–O_2(2)$	3.82		
$C_2(1)–O_1(3)$	3.80		
$C_4(1)–O_1(3)$	3.62		
$C_4(1)–N(3)$	3.93		
$C_4(1)–C_{13}(3)$	3.95		
$C_6(1)–O_3(3)$	3.85		

[a] In ångström units.

for both conjugated and unsaturated π-bonding systems, and not necessarily for $M^+ \cdots C_6H_6$ complexes only, as suggested by Turner and Amma.[26] Such asymmetry has also been found in the case of silver cyclooctatetraene nitrate,[27] in humulene,[28] and in silver–bullvalene complex.[29] The nearest $Ag^+–C$ distances are listed in Table VII along with the comparable distances found in various other crystallographic works.

Table VII

$Ag^+ \cdots C$ distance, Å	Molecule	Ref
2.50	$C_6H_6 \cdot AgClO_4$	*a*
2.63		
2.46	Silver cyclooctatetraene nitrate	27
2.51		
2.78		
2.84		
2.47	$C_6H_6 \cdot AgAlCl_4$	26
2.92		
2.35	$C_{15}H_{24} \cdot 2AgNO_3$–humulene	28
2.43	$(C_{10}H_{10})_3 \cdot AgBF_4$	29
2.33		
2.42		
2.60		
2.65		
2.79		
2.67		
2.85		
2.44	$C_{15}H_{24} \cdot AgNO_3$ β-Gorgonene–silver nitrate	Present work
2.68		
2.47		
2.63		

[a] H. G. Smith and R. E. Rundle, *J. Amer. Chem. Soc.*, **80**, 5075 (1958).

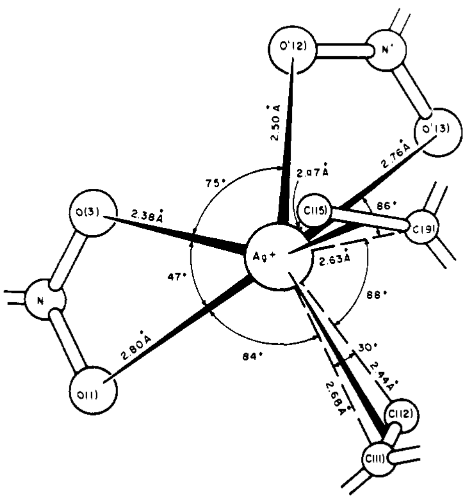

Figure 4. Coordination of silver ion. Solid lines indicate possible bonding.

The observed $Ag^+–O$ distances are well within range of values that have been found in other compounds. Some of these are listed in Table VIII. The distance $Ag^+–O_3$ of 2.38 ± 0.01 Å is shorter than the sum of the ionic radii (2.46 Å) for these two atoms—indicating a strong covalent interaction of the type suggested by Mathews and Lipscomb[27] in the case of silver cyclooctatetraene nitrate.

Table VIII

$Ag^+ \cdots O$ distance, Å	Molecule	Ref
2.66	$C_6H_6 \cdot AgClO_4$	*a*
2.70		
2.68		
3.20		
2.36	Silver cyclooctatetraene nitrate, $AgC_8H_8NO_3$	27
2.43		
2.40	Silver chlorite, $AgClO_2$	*b*
2.60		
2.42	Silver nitrite, $AgNO_2$	*c*
2.73		
2.50	β-Gorgonene–silver nitrate, $C_{15}H_{24} \cdot AgNO_3$	Present work
2.75		
2.38		
2.80		

[a] See Table VII, footnote *a*. [b] J. Cooper and R. E. Marsh, *Acta Cryst.*, **14**, 202 (1961). [c] R. E. Long and R. E. Marsh, *ibid.*, **15**, 448 (1962).

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