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Structure of (*cis,trans,cis*-η-1,5,9-Cyclotridecatriene)nitratosilver(I)

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Abstract. $[Ag(NO_3)(C_{13}H_{20})]$, $M_r = 346{\cdot}2$, monoclinic, $P2_1/c$, $a = 12{\cdot}074\ (2)$, $b = 8{\cdot}071\ (2)$, $c = 14{\cdot}229\ (4)$ Å, $\beta = 93{\cdot}49\ (2)°$, $V = 1384\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}66$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}42$ mm^{-1}, $F(000) = 704$, $T = 293$ K, $R = 0{\cdot}049$ for 2261 independent observed reflections. The Ag atom is five-coordinated by two O atoms of the NO_3^- anion [at 2·471 (5) and 2·555 (5) Å] and by the three double bonds of the triene [at 2·381 (6), 2·473 (6) and 2·357 (6) Å], the geometry of which is described and briefly compared with those of some other unsaturated cyclic hydrocarbons.

Introduction. In recent years strain-energy calculations, NMR spectroscopic investigations at low temperatures and X-ray diffraction studies have provided considerable knowledge about the conformational properties of medium and large cycloalkanes and their derivatives. For the cyclotridecane some low-energy conformations were established (Dale, 1973, 1976; Anet & Rawdah, 1978). To the best of our knowledge no conformational investigations have been made for the parent unsaturated 13-membered ring.

Some biologically active natural products which have been isolated in recent years involve such unsaturated 13-membered rings. Thus the chaetoglobosins A, B and D as well as the 10-*O*-acetylchaetoglobosins A, B, and D, members of the cytochalasins, a group of cytotoxic secondary metabolites of microorganisms, are substituted *trans,trans,trans*-1,5,9-cyclotridecatrienes (Tamm, 1978; Probst & Tamm, 1981). The stereostructure of chaetoglobosin A, a 3-indolyl[13]cytochalasin, was established by X-ray analysis some years ago (Silverton, Akiyama, Kabuto, Sekita, Yoshihira & Natori, 1976).

In connection with our investigations of transannular reactivity of unsaturated medium- and large-ring compounds (Haufe & Mühlstädt, 1984), we are interested in the determination of the structure of such compounds. Presently we wish to report the molecular structure of an Ag complex of the unsubstituted *cis,trans,cis*-1,5,9-cyclotridecatriene.

Experimental. The parent hydrocarbon *cis,trans,cis*-1,5,9-cyclotridecatriene was synthesized by ring enlargement starting from *cis,trans,trans*-1,5,9-cyclododecatriene. The $AgNO_3$ complex was formed by arranging in layers solutions of 169 mg (1 mmol) $AgNO_3$ in 1 ml water and 176 mg (1 mmol) triene in 1 ml tetrachloromethane and storing overnight in the refrigerator. The white precipitate formed was separated and recrystallized from ethanol. Prismatic single crystal, 0·1 × 0·5 × 0·5 mm; Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, ω–θ scan, $1 \le 2\theta \le 64°$. Unit-cell parameters refined from setting angles of 25 selected reflections ($5{\cdot}8 \le 2\theta \le 45{\cdot}1°$). 4076 independent reflections, only 2261 observed according to the two fulfilled conditions: $I > 1{\cdot}43\sigma(I)$ and $I > 1{\cdot}3\ I_{\text{background}}$. $-17 \le h \le 17$, $0 \le k \le 12$, $0 \le l \le 14$. 506 as a standard reflection: 6·5% linear decrease in intensity, appropriate correction applied. Lp corrections, no absorption correction. Patterson function and heavy-atom method. Full-matrix refinements based on F with $w = (a + b|F_o|)^{-2}$ calculated from $|\overline{\Delta F}|$ *vs* $|\overline{F_o}|$ curves. H from ΔF syntheses, with isotropic B equal to B_{eq} of bearing C. Final refinement involving x,y,z,β_{ij} parameters for non-H atoms and x,y,z for H. $R = 0{\cdot}049$, $wR = 0{\cdot}062$, $S = 1{\cdot}023$, $(\Delta/\sigma)_{\max} = 0{\cdot}53$ (non-H atoms), $|\Delta\rho| \le 0{\cdot}74$ e Å^{-3}. f from *International Tables for X-ray Crystallography* (1974). Computing made by means of our library of classical crystallographic programs (Quaglieri, Loiseleur & Thomas, 1972).

Discussion. The refined atomic parameters are given in Table 1.* The drawing of the complex molecule in Fig. 1 was obtained by means of the *ORTEP* program (Johnson, 1965). The Ag atom is coordinated to the O(1) and O(2) atoms of the NO_3^- anion and to each of

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, C—H distances and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42281 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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the three double bonds, C(1)=C(2), C(5)=C(6) and C(9)=C(10). Some main Ag-coordination values are in Table 2. The Ag—O bond lengths are similar to those obtained in some other $AgNO_3$ complexes (Ganis & Dunitz, 1967; Ermer, Eser & Dunitz, 1971; Barrow, Bürgi, Camalli, Caruso, Fischer, Venanzi & Zambonelli, 1982). The Ag coordination bonds involving the double-bonded C atoms, such as they are here expressed, are somewhat different in length according to the *cis* or *trans* configuration around the double bonds: 2·381 (6) and 2·357 (6) Å with the *cis*-type bonds C(1)=C(2) and C(9)=C(10), and 2·473 (6) Å with the *trans*-type bond C(5)=C(6). We may also point out that the Ag—[C(5),C(6)] length is the longest, while the C(5)=C(6) bond which is the sole *trans*-type, is the shortest double bond (Table 3). The Ag—[C(*i*),C(*j*)] bond lengths are to be compared with that of the *trans*-cyclodecene–$AgNO_3$ complex (Ganis & Dunitz, 1967): 2·34 Å with a C=C length of 1·35 (8) Å; and with those of the humulene–$AgNO_3$ adduct (MacPhail & Sim, 1966): Ag(2)—[C(7),C(8)] = Ag(1)—[C(10),C(11)] = 2·29 Å with *trans* C=C lengths respectively equal to 1·28 (4) and 1·40 (4) Å.

Table 1. *Relative atomic coordinates and* B_{eq} *thermal parameters*

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Ag	0·23482 (3)	0·13195 (5)	0·47253 (3)	4·4 (1)
O(1)	0·2965 (4)	−0·0996 (6)	0·5864 (3)	6·1 (2)
O(2)	0·2053 (4)	0·0989 (5)	0·6418 (3)	5·9 (2)
O(3)	0·2719 (5)	−0·0922 (7)	0·7337 (3)	7·1 (2)
N	0·2586 (4)	−0·0323 (5)	0·6558 (3)	4·3 (2)
C(1)	0·4244 (4)	0·2321 (7)	0·4487 (4)	4·5 (2)
C(2)	0·3787 (5)	0·3472 (8)	0·5018 (4)	4·7 (2)
C(3)	0·3280 (5)	0·5091 (7)	0·4710 (5)	5·3 (3)
C(4)	0·2061 (6)	0·5221 (8)	0·4893 (6)	5·9 (2)
C(5)	0·1406 (6)	0·4020 (8)	0·4205 (7)	6·8 (3)
C(6)	0·0614 (6)	0·3098 (9)	0·4406 (7)	6·7 (3)
C(7)	−0·0064 (5)	0·2026 (9)	0·3730 (6)	6·5 (3)
C(8)	0·0519 (6)	0·1004 (9)	0·3023 (5)	5·9 (3)
C(9)	0·1312 (6)	−0·0230 (7)	0·3487 (5)	5·5 (2)
C(10)	0·2387 (6)	−0·0499 (6)	0·3340 (5)	5·2 (3)
C(11)	0·3050 (6)	0·0291 (8)	0·2618 (5)	5·4 (3)
C(12)	0·4245 (5)	0·0754 (9)	0·2931 (5)	5·4 (2)
C(13)	0·4408 (5)	0·2385 (8)	0·3466 (5)	5·0 (2)

Table 2. *Main* Ag *coordination bond lengths* (Å) *and angles* (°)

[C(*i*), C(*j*)] = midpoint of C(*i*) = C(*j*) bond.

Ag—[C(1), C(2)]	2·381 (6)	Ag—[C(9), C(10)]	2·357 (6)
Ag—[C(5), C(6)]	2·473 (6)	Ag—O(1)	2·555 (5)
Ag—O(2)	2·471 (5)		
O(1)—Ag—O(2)	49·9 (1)	O(2)—Ag—[C(9), C(10)]	131·6 (2)
O(1)—Ag—[C(1), C(2)]	99·6 (2)	O(2)—Ag—[C(5), C(6)]	100·6 (2)
O(1)—Ag—[C(9), C(10)]	97·5 (2)	[C(1), C(2)]—Ag—[C(9), C(10)]	119·8 (2)
O(1)—Ag—[C(5), C(6)]	148·1 (2)	[C(1), C(2)]—Ag—[C(5), C(6)]	98·8 (2)
O(2)—Ag—[C(1), C(2)]	102·4 (2)	[C(9), C(10)]—Ag—[C(5), C(6)]	95·7 (2)

Table 3. *Bond lengths* (Å) *and angles* (°) *within the* NO_3 *and* $C_{13}H_{20}$ *ligands*

N—O(1)	1·239 (6)	N—O(2)	1·249 (6)
N—O(3)	1·210 (6)	C(1)=C(2)	1·337 (9)
C(2)—C(3)	1·497 (9)	C(3)—C(4)	1·514 (9)
C(4)—C(5)	1·559 (9)	C(5)=C(6)	1·258 (9)
C(6)—C(7)	1·499 (9)	C(7)—C(8)	1·508 (9)
C(8)—C(9)	1·506 (9)	C(9)=C(10)	1·345 (9)
C(10)—C(11)	1·485 (9)	C(11)—C(12)	1·531 (9)
C(12)—C(13)	1·527 (9)	C(13)—C(1)	1·479 (9)
O(1)—N—O(2)	117·1 (5)	O(1)—N—O(3)	121·3 (5)
O(2)—N—O(3)	121·6 (5)	C(2)—C(1)—C(13)	127·9 (5)
C(1)—C(2)—C(3)	128·1 (6)	C(2)—C(3)—C(4)	113·3 (5)
C(3)—C(4)—C(5)	108·1 (6)	C(4)—C(5)—C(6)	126·1 (9)
C(5)—C(6)—C(7)	126·1 (9)	C(6)—C(7)—C(8)	119·0 (6)
C(7)—C(8)—C(9)	112·3 (6)	C(8)—C(9)—C(10)	129·2 (6)
C(9)—C(10)—C(11)	127·2 (6)	C(10)—C(11)—C(12)	116·2 (6)
C(11)—C(12)—C(13)	116·5 (5)	C(1)—C(13)—C(12)	116·0 (5)

The 1,5,9-cyclotridecatriene ring possesses a *CT*-conformation (Figs. 1 and 2) in the definition of Sutherland (1974). There is a small torsion of the double bonds: only 4° for the *trans* configurated C(5)=C(6) and 3 and 5° respectively for the *cis* C(1)=C(2) and C(9)=C(10) bonds. This result is comparable with derivatives of other large-ring compounds such as cembrene (Drew, Templeton & Zalkin, 1969; Raldugin, Yaroshenko & Gatilov, 1981), a natural 14-membered diterpenic *trans,cis,trans,-trans*-tetraene, or the *trans,trans,trans*-1,5,9-cyclo-

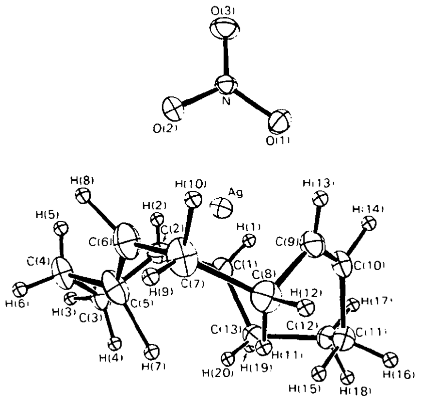

Fig. 1. *ORTEP* view of the Ag complex with 15% probability thermal ellipsoids. (The H atoms are arbitrarily scaled.)

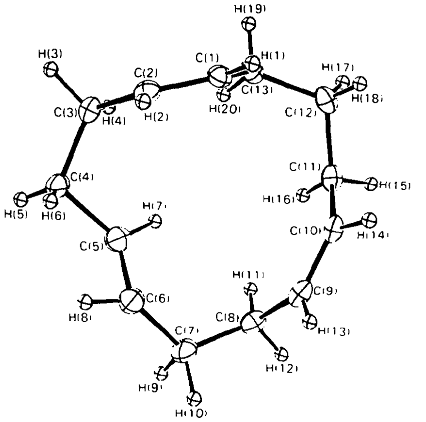

Fig. 2. Another *ORTEP* view showing only the triene ligand (on the same scale as in Fig. 1).

dodecatriene in which the torsion angles are between 2 and 4° (Allegra & Bassi, 1962; Immirzi & Allegra, 1967). In medium-sized rings the torsion angles are usually larger. However, in some derivatives of the sesquiterpene humulene, a *trans,trans,trans*-1,4,8-cycloundecatriene, angles of 8 to 23° were obtained (MacPhail & Sim, 1966; Hall, Nimgirawath, Raston, Sittatrakul, Thadaniti, Thirasasana & White, 1981; Russell, Sim & White, 1982; MacAlpine, Porte & Sim, 1982; Khan, MacAlpine, Porte & Sim, 1983). In a *trans*-oxacycloundecene derivative we found 10°, while in a related *cis*-oxacycloundecene a value of only 3° was obtained (Sieler, Richter, Haufe, Lindqvist, Andersen & Faure, 1985; Sim & Haufe, 1984, unpublished results). In the *cis,trans*-1,5-cyclodecatriene–$AgNO_3$ complex the *cis* double bond is also nearly planar, while the *trans*-double-bond torsion is 22° (Rogers & Smart, 1969). Related values were found in some natural 10-membered-ring sesquiterpenes involving the *cis,trans*-1,5-diene system (Rychlewska, 1982; Matsuo, Nozaki, Kubota, Uto & Nakayama, 1984). Even larger torsion angles were obtained in *trans*-cyclodecene derivatives (Ganis & Dunitz, 1967; Ermer, 1970) and in *trans*-cyclooctene derivatives (up to 44°) (Ermer & Mason, 1982), while in *cis*-cyclodecenes only a small torsion was found (Ermer *et al.,* 1971).

The lengths of the *cis*-type double bonds of 1·337 (9) and 1·345 (9) Å agree with those usually obtained for nearly planar double bonds in other cyclic systems (Ermer *et al.,* 1971; Rychlewska, 1982; Matsuo *et al.,* 1984) and in propene where a value of 1·334 (4) Å was found by gas-electron-diffraction study (Tokue, Fukuyama & Kuchitsu, 1973). For the *trans*-type bond a very short length of 1·258 (9) Å is obtained. Such a short length was encountered in *trans*-civetton-2,4-dinitrophenylhydrazone (Bernardinelli & Gerdil, 1982) [1·275 (12) Å]. The lengths of the C—C σ bonds are as expected.

The transannular H···H distances of the vinylic H atoms: H(2)···H(8) = 3·7 (1) and H(1)···H(14) = 3·5 (1) Å, are close to that found in the *trans,trans,trans*-1,5,9-cyclododecatriene: 3·6 Å (Immirzi & Allegra, 1967). All other transannular distances of vinylic H atoms are greater than 4 Å. Thus, there are no transannular interactions between the vinylic H atoms.

Some shorter distances are obtained for some 1,3-H atoms, *e.g.* H(6)···H(8) = 2·5 (1), H(4)···H(7) = 2·4 (1) Å as well as 1,4-H atoms: H(4)···H(20) = 2·2 (1), H(7)···H(11) = 2·4 (1) Å.

The transannular distances between the sp^2-hybridized C atoms in 1,4-positions are: C(6)···C(9) = 3·12 (1) and C(2)···C(5) = 3·065 (9) Å, and in 1,5-positions: C(1)···C(5) = 3·690 (8), C(5)···C(9) = 3·579 (9), C(1)···C(10) = 3·525 (8) and C(6)···C(10) = 3·96 (1) Å. These values are similar to those found in *trans,trans,trans*-1,5,9-cyclododecatriene: 3·0 Å for the 1,4-position and 3·5 and 3·6 Å respectively for the 1,5-positions. All transannular distances of 1,6-positions are larger than 4 Å.

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