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METAL π-COMPLEXES OF CYCLOOCTATETRAENES

II*. CRYSTAL AND MOLECULAR STRUCTURE OF BIS(1-2:5-6-η-CYCLOOCTATETRAENE)SILVER(I) NITRATE, $(C_8H_8)_2AgNO_3$

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Summary

X-ray analysis showed that the 2 : 1 adduct of cyclooctatetraene and silver nitrate exists as discrete $(C_8H_8)_2AgNO_3$ molecules in the crystalline state. Each molecule has C_2 symmetry, with the Ag^I ion coordinated by a symmetrical bidentate nitrato group and four double bonds, two from each cyclooctatetraene moiety in an unsymmetrical mode. This overcrowded coordination geometry leads to significantly weaker metal–ligand interactions than in the previously studied 1 : 1 adduct and related cyclic oligoolefin-silver(I) complexes.

Crystals are monoclinic, space group $C2/c$, with $a = 10.296(2)$, $b = 9.752(1)$, $c = 15.122(4)$ Å, $\beta = 95.59(2)°$, and $Z = 4$. The structure was refined anisotropically to $R = 0.035$ for 1395 Mo-K_α data.

Introduction

Cyclooctatetraene (C_8H_8, COT) reacts with silver nitrate to form, in increasing order of stability, three adducts of compositions $2COT \cdot AgNO_3$, $COT \cdot AgNO_3$, and $2COT \cdot 3AgNO_3$ [1]. An early X-ray crystallographic study of the 1 : 1 adduct [2,3] revealed a chain-and-layer structure with each Ag^I coordinated by two O atoms (belonging to different nitrato groups), two non-adjacent double bonds of a COT molecule, and a more distant double bond from a COT molecule in the next unit cell. A recent reinvestigation of this structure using new Mo-K_α diffractometer data has rectified all the unsatisfactory aspects [4] of the previous work and elucidated the intricacies of all the Ag^I–ligand interactions and ligand distortions [5]. In the present study, we prepared single crystals of the 2 : 1 adduct and carried out an X-ray analysis to clarify the modes of coordination of the COT and nitrato groups around the Ag^I ion.

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* For part I see ref. 5

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Experimental

Preparation of $(C_8H_8)_2AgNO_3$

The literature method [1] gave a polycrystalline product in the form of yellow granules. In our modified procedure, reagent grade silver nitrate (2.0 g, 11.8 mmol) dissolved in 20 ml H_2O was shaken with COT (Aldrich) (3 ml, 26.7 mmol) in a stoppered conical flask for 15 min using a mechanical shaker. The transparent plate-shaped crystals of the 2 : 1 adduct floating on the surface of the mother liquor were found to be suitable for diffraction use. Upon exposure to air, the adduct instantly turns opaque while emitting a strong smell of COT vapor.

Data collection

A sample was removed from the mother liquor and quickly covered with petroleum jelly. A single crystal with dimensions of 0.4 × 0.4 × 0.3 mm was selected and sealed in a 0.5 mm diameter Lindemann glass capillary partly filled with liquid COT at the tip portion. The crystal was thus enclosed in a COT atmosphere, and the petroleum jelly held it stationary on the wall of the glass capillary. Data were collected on a Nicolet R3m automated four-circle diffractometer with graphite-monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å). The intensities of 1728 unique reflections with $0° \leqslant 2\theta \leqslant 54°$ were recorded using the θ–2θ scan mode. Three standards measured every 50 reflections showed only small random deviations within ±2% of their mean values. In addition to Lorentz and polarization factors, absorption correction (mean $\mu r = 0.24$, transmission factors 0.574 to 0.435) was applied using an empirical method based on a pseudo-ellipsoidal treatment of reflection intensity measurements at different azimuthal angles. Other details of the experimental procedure have been noted [5].

Crystal data

$(C_8H_8)_2AgNO_3$, $M = 378.18$, monoclinic, space group $C2/c$ (from systematic absences and intensity statistics), $a = 10.296(2)$, $b = 9.752(1)$, $c = 15.122(4)$ Å, $\beta = 95.59(2)°$, $U = 1511.1(6)$ Å^3, $Z = 4$, $D_c = 1.662(7)$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 13.28$ cm^{-1}.

Structure solution and refinement

Space group symmetry considerations require that the Ag^I ion and one N–O bond in the nitrato group lie on a crystallographic two-fold axis. Direct phase determination readily revealed the position of the metal atom. The remaining eleven non-hydrogen atoms appeared in a subsequent electron-density map. These twelve atoms were refined anisotropically to a conventional R index of 0.049. The hydrogen atoms were next generated on the basis of sp^2 hybridization of their respective bonded carbon atoms, and were assigned fixed isotropic temperature factors. Convergence was reached at $R = 0.035$ for 1395 observed reflections with $I > 1.5\sigma(I)$. The final difference map was essentially flat, the highest residual peak being 0.38 e Å^{-3}.

All computations were carried out on a Nova 3 minicomputer with the SHELXTL program package [6]. Complex neutral-atom scattering factors [7] were employed. The weighting scheme employed for the blocked-cascade least-squares refinement and analysis of variance was $w = [\sigma^2(F) + 0.0005|F|^2]^{-1}$. An empirical isotropic

TABLE 1

FRACTIONAL ATOMIC COORDINATES[a] ($\times 10^5$ for Ag, $\times 10^4$ FOR OTHER ATOMS) AND THERMAL PARAMETERS[b] (Å$^2 \times 10^4$ for Ag, $\times 10^3$ FOR OTHER ATOMS)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq} or U_{iso}
Ag	0	30478(4)	1/4	847(4)	492(3)	474(2)	0	63(2)	0	605(2)
N	0	6048(5)	1/4	81(3)	45(2)	60(3)	0	8(2)	0	62(2)
O(1)	0	7312(5)	1/4	211(8)	41(3)	165(7)	0	52(6)	0	137(4)
O(2)	−904(3)	5390(3)	2779(3)	72(2)	69(2)	114(3)	0(2)	39(2)	3(2)	83(1)
C(1)	1357(4)	3257(4)	4122(3)	50(2)	57(2)	51(2)	1(2)	0(2)	−6(2)	53(1)
C(2)	1807(4)	2121(4)	3768(3)	44(2)	78(3)	48(2)	−3(2)	4(1)	8(2)	57(1)
C(3)	1390(5)	719(4)	3932(3)	85(3)	55(2)	53(2)	1(2)	1(2)	27(2)	65(1)
C(4)	196(5)	226(4)	3809(3)	109(4)	40(2)	50(2)	2(2)	12(2)	−2(2)	66(2)
C(5)	−978(4)	986(4)	3469(2)	69(2)	63(2)	47(2)	0(2)	6(2)	−25(2)	60(1)
C(6)	−1426(4)	2130(4)	3812(3)	45(2)	80(3)	53(2)	5(2)	9(2)	−12(2)	59(1)
C(7)	−843(4)	2847(4)	4610(2)	57(2)	65(3)	46(2)	0(2)	16(2)	6(2)	55(1)
C(8)	357(4)	3312(4)	4746(2)	65(3)	49(2)	46(2)	−6(1)	5(2)	6(2)	53(1)
H(1)	1720	4113	3952							70
H(2)	2469	2233	3368							70
H(3)	2060	89	4154							70
H(4)	82	−721	3956							70
H(5)	−1469	625	2949							70
H(6)	−2201	2525	3510							70
H(7)	−1393	2985	5079							70
H(8)	603	3733	5311							70

[a] The hydrogen atoms are numbered according to their parent carbon atoms. [b] Anisotropic temperature factor expression: $T = \exp[-2\pi^2 \Sigma\Sigma a_i^\star a_j^\star h_i h_j U_{ij}]$. U_{eq} is the equivalent isotropic temperature factor calculated as one-third of the trace of the orthogonalised U_{ij} matrix.

TABLE 2

BOND LENGTHS (Å), BOND ANGLES (deg) AND TORSION ANGLES (deg) [a]

Ag-O(2)	2.518(3)	C(1)-C(2)	1.334(6)
Ag-C(1)	2.710(4)	C(2)-C(3)	1.461(6)
Ag-C(2)	2.694(4)	C(3)-C(4)	1.316(7)
Ag-C(5)	2.737(4)	C(4)-C(5)	1.467(6)
Ag-C(6)	2.731(4)	C(5)-C(6)	1.331(6)
N-O(1)	1.232(7)	C(6)-C(7)	1.471(5)
N-O(2)	1.239(4)	C(7)-C(8)	1.313(6)
		C(8)-C(1)	1.463(6)
O(1)-N-O(2)	121.2(2)	C(3)-C(4)-C(5)	126.2(4)
O(2)-N-O(2)^{I}	117.6(5)	C(4)-C(5)-C(6)	126.3(4)
C(8)-C(1)-C(2)	125.7(4)	C(5)-C(6)-C(7)	126.0(4)
C(1)-C(2)-C(3)	126.1(4)	C(6)-C(7)-C(8)	126.5(4)
C(2)-C(3)-C(4)	127.1(4)	C(7)-C(8)-C(1)	126.6(3)
C(8)-C(1)-C(2)-C(3)	0.1(6)	C(4)-C(5)-C(6)-C(7)	−1.0(7)
C(1)-C(2)-C(3)-C(4)	56.8(6)	C(5)-C(6)-C(7)-C(8)	56.8(6)
C(2)-C(3)-C(4)-C(5)	0.7(7)	C(6)-C(7)-C(8)-C(9)	2.2(6)
C(3)-C(4)-C(5)-C(6)	−56.8(7)	C(7)-C(8)-C(1)-C(2)	−58.7(6)
Trigonal bipyramidal coordination geometry			
Ag-M_{12}	2.619	Ag-M_{56}	2.652
M_{56}-Ag-M^{I}_{56}	113.6	M_{12}-Ag-M_{56}	71.1
M_{12}-Ag-N	97.7	M_{12}-Ag-M^{I}_{56}	100.2
		M_{12}-Ag-M^{I}_{12}	164.7

[a] Roman numeral I denotes the transformation $-x, y, 1/2-z$. M_{ij} represents the center of the C(i)-C(j) double bond.

extinction parameter ε in the expression [6]

$$F_{\mathrm{corr}} = F_{\mathrm{c}}\left(1 + \varepsilon F_{\mathrm{c}}^{2}/\sin 2\theta\right)^{-1/4}$$

was varied and has the value 1.88×10^{-6}.

The final positional and thermal parameters for the non-hydrogen atoms are given in Table 1, in accordance with the labelling scheme of Fig. 1. Molecular dimensions and torsion angles are listed in Table 2, and least-squares planes through selected sets of atoms in Table 3 *.

Results and discussion

The crystal structure is built up by a packing of discrete molecules corresponding to the formula $(C_8H_8)_2AgNO_3$ (Fig. 2). Each molecule lies on a crystallographic diad, with the Ag^{I} ion coordinated by a symmetrical bidentate nitrato group [8] and four double bonds, two from each COT moiety in an unsymmetrical fashion (Fig. 1). If the bidentate nitrato group is considered to occupy one position in the coordination sphere, the configuration about Ag^{I} can be described as approximately trigonal bipyramidal: the nitrato group and the centers of the C(5)-C(6) and C(5)^{I}-C(6)^{I}

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* Tables of observed and calculated structure factors are available from the authors on request.

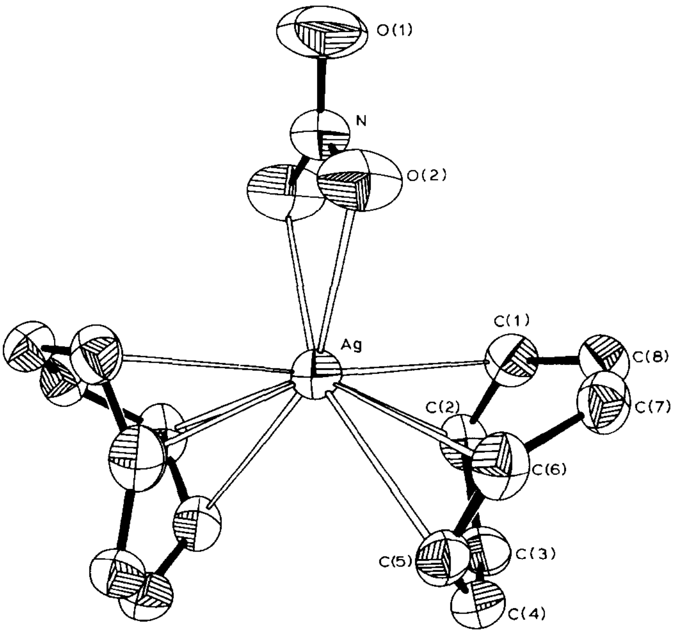

Fig. 1. Perspective view of the $(C_8H_8)_2AgNO_3$ molecule, showing the atom labelling scheme and thermal ellipsoids at the 40% probability level. Metal–ligand atom interactions are represented by open bonds.

double bonds lie in the equatorial plane, and the pair of C(1)–C(2) and $C(1)^I$–$C(2)^I$ double bonds occupy the axial positions (Table 2).

Athough a large number of Ag^I complexes of cyclic di- and oligo-olefins have been synthesized [9], well-characterized entities containing three or more olefinic ligands in the coordination sphere are rare. Known examples include the tribullvalene adduct $(C_{10}H_{10})_3AgBF_4$ [10] and the di-1,5-cyclooctadiene adduct $(C_8H_{12})_2AgBF_4$ [11]. In the first complex, the three bullvalene molecules are arranged approximately trigonally about the Ag^I ion: two of these have one double

TABLE 3

LEAST-SQUARES PLANES [a]

Plane	Atoms	*A*	*B*	*C*	*D*	rmsΔ ($\times 10^4$Å)
1	C(1), C(2), C(5), C(6)	0.1051	−0.4202	0.9013	4.3026	48
2	C(2), C(3), C(4), C(5)	−0.1553	0.2538	0.9547	5.5029	20
3	C(6), C(7), C(8), C(1)	0.3120	−0.8785	0.3619	−0.1464	63
4	C(3), C(4), C(7), C(8)	0.1061	−0.4243	0.8993	5.0827	75
5	C(8), C(1), C(2), C(3)	0.7096	−0.0727	0.7008	5.0293	3
6	C(4), C(5), C(6), C(7)	−0.5512	−0.5506	0.6269	3.3686	31

Angles between planes: 1–2, 42.5°; 1–3, 43.3°; 4–5, 42.6°; 4–6, 42.4°.

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[a] Plane equation is of the form $AX+BY+CZ=D$, where X, Y, Z are orthogonal coordinates in Å referred to axes x_0, y_0, z_0 respectively, with x_0 parallel to $\boldsymbol{a}^\star$, y_0 to $\boldsymbol{c}\times\boldsymbol{a}^\star$, with z_0 to $\boldsymbol{c}$.

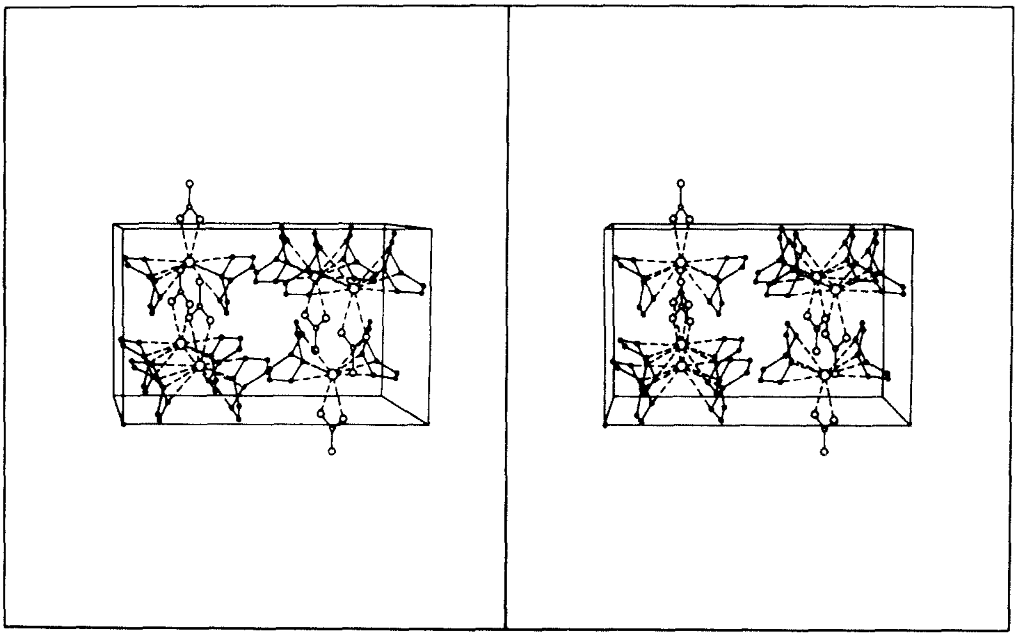

Fig. 2. Stereo drawing showing the packing of discrete $(C_8H_8)_2AgNO_3$ units. The unit cell origin lies at the lower left corner, with *a* pointing away from the reader, *b* upwards, and *c* from left to right.

bond each coordinated to the metal center (mean Ag–C = 2.66 Å), while the third is oriented such that two of its double bonds are equidistant from the metal atom (Ag–C = 2.42 Å). In the di-1,5-cyclooctadiene complex, the Ag^I ion is embraced by the chelating arms of two diolefin ligands (mean Ag–C = 2.50 Å) in a modified tetrahedral geometry described as "cubical" [12]. As compared to these two four-coordinate Ag^I-olefin complexes, the present adduct has an additional symmetrically bidentate nitrato ligand which necessarily causes an expansion of the coordination sphere around the metal center. The significantly longer observed Ag^I–ligand distances (Table 2), also with reference to those in the 1 : 1 adduct [5], substantiate this expectation and provide a rationale for the relative instability of the 2 : 1 adduct.

The conformation of the present coordinated COT moiety (Tables 2 and 3) is less distorted from the idealized D_{2d} geometry (C–C 1.476 Å, C=C 1.340 Å, bond angle $\theta = 126.1°$, torsion angle about C–C $\omega = 57.9°$, dihedral angle $\alpha = 43.2°$) of free COT [13] than that in the 1 : 1 adduct. Bond lengths in the cyclic polyolefin are, however, virtually identical in the two adducts, and the order single bond > coordinated double bond > un-coordinated double bond is clearly discernible [Table 2].

For the vast majority of inorganic coordination compounds containing symmetrically bidentate nitrato groups, the terminal N–O bond is invariably shorter than the other two, and the O–N–O angle involving both coordinated oxygen atoms significantly less than 120° [8]. This generalization needs modification for symmetrically bidentate nitratosilver(I) complexes which also contain organic ligands, mainly due to a weakening of metal–oxygen bonding. Thus in $AgNO_3 \cdot P(C_6H_5)_3$ [14], the coordinated nitrato group remains undistorted from the values in the nitrate ion

(N–O = 1.245 Å, O–N–O = 120°) [8], while only angular distortion is observed in $AgNO_3 \cdot (CH_2)_6N_4$ [15] and in the present adduct.

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