

METAL π -COMPLEXES OF CYCLOOCTATETRAENES

I. REINVESTIGATION OF THE CRYSTAL STRUCTURE OF THE 1:1 ADDUCT OF CYCLOOCTATETRAENE AND SILVER NITRATE

WOON CHEUNG HO and THOMAS C.W. MAK *

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories (Hong Kong)

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Summary

Redetermination of the crystal structure of $C_8H_8 \cdot AgNO_3$ from new $Mo-K_\alpha$ diffractometer data has rectified all the unsatisfactory aspects of the previous study. The structure consists of strongly-bonded $Ag^I-C_8H_8$ units linked by weaker metal–ligand interactions to form infinite chains parallel to the c axis; neighboring chains are cross-linked by bridging nitrate groups to form corrugated sheets normal to the a axis. Crystals are monoclinic, space group $P2_1/a$, with $a = 16.796(3)$, $b = 8.932(2)$, $c = 5.860(1)$ Å, $\beta = 90.72(1)^\circ$, and $Z = 4$. The structure was refined to a conventional R value of 0.039 for 1382 unique observed data.

Introduction

The formation of crystalline adducts of cyclooctatetraene (C_8H_8 , COT) with salts of Group IB metals was first reported by Reppe and coworkers [1]. Subsequently, Cope and Hochstein [2] established that COT reacts with aqueous silver nitrate to give at least three distinct addition compounds with compositions corresponding to $2COT \cdot AgNO_3$, $COT \cdot AgNO_3$ and $2COT \cdot 3AgNO_3$. X-ray analysis of the 1:1 adduct provided the first elucidation of the π bonding between a cyclic polyolefin and a heavy metal ion [3,4]. This early study was based on visual data recorded on Weissenberg and precession photographs, mostly with $Mo-K_\alpha$ radiation. Structure refinement (anisotropic for Ag, isotropic for the lighter non-hydrogen atoms) yielded a conventional R index of 0.112, but a number of unexplained peaks, some of heights comparable to that of a carbon atom, were located in the Patterson superposition function, in a difference synthesis, and in the final electron-density map (see Fig. 1 in [4]). In order to ascertain the correctness of this historically

* Correspondence to this author.

significant structure, we deemed it worthwhile to perform an analysis with more accurate diffractometer data. The precise structural information obtained herein will be of interest in comparison with those gathered in our current studies of the 2 : 1 and 2 : 3 adducts.

Experimental

Preparation of $C_8H_8 \cdot AgNO_3$

The adduct was prepared according to the published procedure [2] with minor modifications. Reagent grade silver nitrate (2.0 g, 11.8 mmol) dissolved in 5 ml H_2O was shaken with COT (Aldrich) (2 ml, 17.8 mmol) and ligroin (5 ml). The resulting pale yellow crystalline precipitate was redissolved by warming the mixture to 50°C, and on slow cooling needle-shaped crystals were deposited. The adduct decomposes gradually to $2COT \cdot 3AgNO_3$ by loss of COT [2] and must be freshly prepared prior to the diffraction study.

Data collection

Crystals of the 1 : 1 adduct occur as needles elongated along *c* with the (100) face well developed. A clear plate with approximate dimensions $0.08 \times 0.36 \times 0.44$ mm was sealed in a 0.5 mm diameter Lindemann glass capillary under a COT atmosphere. Unit-cell dimensions were determined from least-squares treatment of 16 high-angle reflections measured on a Nicolet R3m diffractometer. Intensities were measured using the θ - 2θ scan technique with three standard reflections monitored periodically to check crystal stability. These check reflections lost about 3% of their initial intensities during the course of the data collection, and a linear decay correction was made. In addition to Lorentz and polarization factors, absorption correction was applied using an empirical method based on a pseudo-ellipsoidal treatment of reflection intensity measurements at different azimuthal angles. Information concerning data measurement and refinement are summarized in Table 1.

Structure refinement

Refinement of the published set of atomic parameters [4] converged to $R = 0.061$ after four least-squares cycles. When the twelve C, N and O atoms were also varied anisotropically, R was further reduced to 0.046. Of the nine highest peaks in the resulting difference map, seven could be identified as hydrogen atoms. In the last stage of refinement, all eight H atoms were included with assigned isotropic temperature factors of 0.06 \AA^2 , and the final difference map contained three residual peaks (0.64 – $0.78 e \text{ \AA}^{-3}$) in the neighbourhood of the Ag^I ion.

All computations were performed with the SHELXTL package of crystallographic programs on a Nova 3 minicomputer [5]. 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 extinction parameter ϵ in the expression [5]

$$F_{\text{corr}} = F_c / (1 + \epsilon F_c^2 / \sin 2\theta)^{1/4}$$

was treated as an additional variable (Table 1).

The final positional and thermal parameters are given in Table 2 in accordance

TABLE 1
DATA COLLECTION AND PROCESSING PARAMETERS

| | |
|---|--|
| Molecular formula | $C_8H_8 \cdot AgNO_3$ |
| Molecular weight | 274.03 |
| Cell constants | $a = 16.796(3) \text{ \AA}$ $b = 8.932(2) \text{ \AA}$ $c = 5.860(1) \text{ \AA}$ $\beta = 90.72(1)^\circ$ $V = 879.1(3) \text{ \AA}^3$ $Z = 4$ |
| Density (calcd.) | $\rho = 2.071(1) \text{ g cm}^{-3}$ |
| Space group | $P2_1/a(C_{2h}^5, \text{No.14})$ |
| Radiation | graphite-monochromatized Mo- K_α , $\lambda = 0.71069 \text{ \AA}$ |
| Mean μ | 0.26 |
| Transmission factors | 0.392 to 0.591 |
| Scan type and speed | $\theta-2\theta$, 2.5 to 8 deg min^{-1} |
| Scan range | 1° below K_{α_1} to 1° above K_{α_2} |
| Background counting | stationary counts for 1/2 of scan time at each end of scan |
| Collection range | $\pm h, k, l$; $0^\circ \leq 2\theta \leq 54^\circ$ |
| Unique data measured | 1607 |
| Observed data with $I > 1.5\sigma(I)$ | 1382 |
| Number of variables | 119 |
| Extinction parameter ϵ | 3.02×10^{-6} |
| $R = \sum F_o - F_c / \sum F_o $ | 0.039 |
| Weighting scheme | $w = [\sigma^2(F) + 0.0005 F ^2]^{-1}$ |
| $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$ | 0.038 |
| Goodness of fit | 1.336 |

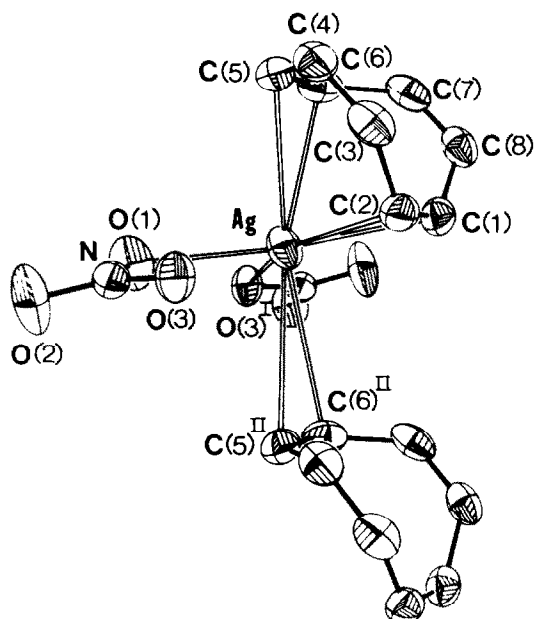


Fig. 1. A perspective view of the configuration around a silver(I) ion in $COT \cdot AgNO_3$, showing the atom labelling scheme and thermal ellipsoids at the 40% probability level. Metal-ligand atom interactions are represented by open bonds.

TABLE 2
 FRACTIONAL ATOMIC COORDINATES^a AND THERMAL PARAMETERS^b ($\text{\AA}^2 \times 10^4$ for Ag; $\times 10^3$ for the other atoms)

| Atom | x | y | z | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} | U_{eq} or U_{iso} |
|------|------------|------------|------------|----------|----------|----------|----------|----------|----------|-------------------------------------|
| Ag | 0.31569(2) | 0.21748(4) | 0.09623(8) | 446(2) | 434(2) | 685(3) | -120(2) | -122(2) | -3(2) | 523(1) |
| N | 0.1624(2) | 0.3834(4) | -0.0067(7) | 42(2) | 41(2) | 44(2) | 4(2) | 2(2) | 2(2) | 42(1) |
| O(1) | 0.1727(3) | 0.2493(4) | 0.0484(9) | 65(3) | 34(2) | 101(3) | 13(2) | -9(2) | 1(2) | 67(2) |
| O(2) | 0.0970(2) | 0.4327(5) | -0.0611(9) | 42(2) | 77(3) | 145(4) | 37(3) | -19(3) | 4(2) | 88(2) |
| O(3) | 0.2213(2) | 0.4686(4) | -0.0046(6) | 41(2) | 44(2) | 73(3) | 4(2) | 1(2) | -10(2) | 53(1) |
| C(1) | 0.4551(3) | 0.2970(6) | 0.1737(9) | 40(3) | 56(3) | 52(3) | -14(2) | 5(2) | -7(2) | 49(2) |
| C(2) | 0.4120(3) | 0.4228(6) | 0.1643(8) | 46(3) | 49(3) | 41(3) | -1(2) | 4(2) | -9(2) | 45(2) |
| C(3) | 0.3844(3) | 0.5074(5) | 0.3653(9) | 59(3) | 33(2) | 59(3) | -5(2) | -15(3) | -2(2) | 51(2) |
| C(4) | 0.3409(3) | 0.4567(6) | 0.5326(9) | 53(3) | 50(3) | 51(3) | -26(2) | -6(2) | 13(2) | 51(2) |
| C(5) | 0.3088(3) | 0.3050(6) | 0.5521(8) | 50(3) | 73(4) | 40(3) | -8(2) | 6(2) | -7(3) | 54(2) |
| C(6) | 0.3522(4) | 0.1794(6) | 0.5609(8) | 73(4) | 46(3) | 42(3) | 1(2) | 0(3) | -11(3) | 54(2) |
| C(7) | 0.4385(4) | 0.1688(6) | 0.5464(9) | 68(4) | 42(3) | 53(3) | -11(2) | -23(3) | 16(3) | 54(2) |
| C(8) | 0.4823(3) | 0.2183(6) | 0.3803(10) | 40(3) | 53(3) | 64(3) | -20(3) | -12(2) | 11(2) | 53(2) |
| H(1) | 0.4699 | 0.2537 | 0.0303 | | | | | | | 60 |
| H(2) | 0.3978 | 0.4610 | 0.0161 | | | | | | | 60 |
| H(3) | 0.4000 | 0.6107 | 0.3739 | | | | | | | 60 |
| H(4) | 0.3292 | 0.5254 | 0.6537 | | | | | | | 60 |
| H(5) | 0.2519 | 0.2947 | 0.5590 | | | | | | | 60 |
| H(6) | 0.3237 | 0.0871 | 0.5788 | | | | | | | 60 |
| H(7) | 0.4658 | 0.1207 | 0.6712 | | | | | | | 60 |
| H(8) | 0.5386 | 0.2014 | 0.3949 | | | | | | | 60 |

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

TABLE 3

BOND LENGTHS (Å), BOND ANGLES (deg) AND TORSION ANGLES (deg)^a

| | | | |
|-------------------------|----------|---------------------|----------|
| Ag-O(1) | 2.431(5) | N-O(1) | 1.252(5) |
| Ag-O(3) ^I | 2.368(3) | N-O(2) | 1.223(6) |
| Ag-C(1) | 2.483(5) | N-O(3) | 1.247(6) |
| Ag-C(2) | 2.475(5) | C(1)-C(2) | 1.338(7) |
| Ag-C(5) | 2.787(5) | C(2)-C(3) | 1.478(7) |
| Ag-C(6) | 2.805(5) | C(3)-C(4) | 1.311(8) |
| Ag...C(5) ^{II} | 3.284(5) | C(4)-C(5) | 1.464(7) |
| Ag...C(6) ^{II} | 3.222(5) | C(5)-C(6) | 1.339(8) |
| | | C(6)-C(7) | 1.455(9) |
| | | C(7)-C(8) | 1.305(8) |
| | | C(8)-C(1) | 1.468(8) |
| O(1)-N-O(2) | 122.2(4) | C(3)-C(4)-C(5) | 126.0(5) |
| O(1)-N-O(3) | 118.3(4) | C(4)-C(5)-C(6) | 125.2(5) |
| O(2)-N-O(3) | 119.5(4) | C(5)-C(6)-C(7) | 126.5(5) |
| C(8)-C(1)-C(2) | 126.8(5) | C(6)-C(7)-C(8) | 126.4(5) |
| C(1)-C(2)-C(3) | 124.9(5) | C(7)-C(8)-C(1) | 127.2(5) |
| C(2)-C(3)-C(4) | 127.0(5) | | |
| C(8)-C(1)-C(2)-C(3) | -0.8(9) | C(4)-C(5)-C(6)-C(7) | 2.0(8) |
| C(1)-C(2)-C(3)-C(4) | 56.7(8) | C(5)-C(6)-C(7)-C(8) | 56.9(8) |
| C(2)-C(3)-C(4)-C(5) | 1.7(9) | C(6)-C(7)-C(8)-C(1) | -0.9(9) |
| C(3)-C(4)-C(5)-C(6) | -60.2(8) | C(7)-C(8)-C(1)-C(2) | -56.0(9) |

^a Roman numerals as superscripts denote the following transformations: I. $1/2 - x, -1/2 + y, -z$; II. $x, y, -1 + z$.

with the atom labelling scheme in Fig. 1*. Bond lengths, bond angles, and torsion angles are listed in Table 3, and least-squares planes through selected sets of atoms in Table 4.

Results and discussion

The present analysis confirmed the principal findings of the previous study [3,4]. The Ag^I-olefin interactions fall into three distinct types: C(1) and C(2) bond to the metal center at an average distance of 2.479 Å, followed by C(5) and C(6) at 2.796 Å, and by C(5)^{II} and C(6)^{II} at 3.253 Å from the COT molecule below (Fig. 1). The first type is in accord with Ag^I-olefin distances in the range 2.48–2.52 Å found in dicycloocta-1,5-dienesilver(I) tetrafluoroborate [6], and the slightly longer second type can be accounted for by the fact that the double bond at the 5-position serves as a bridging ligand. The third type represents an unusually weak π interaction which join the strongly bonded Ag^I-COT units into infinite chains parallel to the *c* axis. Neighboring chains are cross-linked by bridging nitrate groups to form corrugated sheets normal to the *a* axis (Fig. 2). Chains of AgNO₃ units zigzag in the direction of the *b* axis, and this type of chain-and-layer arrangement has been recognised as a common feature in nitrate Ag^I complexes [7,8].

The configuration of the ligands about Ag^I may be described as distorted trigonal bipyramidal, with two metal-oxygen bonds (to different nitrate groups) and the

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

TABLE 4
LEAST-SQUARES PLANES^a

| Plane | Atoms | A | B | C | D | rms Δ ($\times 10^{-4}$ Å) |
|-------|---|---------|---------|--------|---------|------------------------------------|
| 1 | C(1), C(2), C(5), C(6) | 0.6091 | 0.4258 | 0.6691 | 6.4589 | 8 |
| 2 | C(2), C(3), C(4), C(5) | 0.8181 | -0.2784 | 0.5032 | 5.0813 | 48 |
| 3 | C(6), C(7), C(8), C(1) | 0.0883 | 0.8767 | 0.4729 | 3.4791 | 26 |
| 4 | C(3), C(4), C(7), C(8) | 0.6206 | 0.4166 | 0.6643 | 7.3012 | 11 |
| 5 | C(8), C(1), C(2), C(3) | 0.8433 | 0.5374 | 0.0010 | 7.8588 | 22 |
| 6 | C(4), C(5), C(6), C(7) | 0.0557 | 0.0692 | 0.9960 | 3.7045 | 57 |
| 7 | Ag, C(1), C(2), O(1), O(3) [†] | -0.1273 | -0.1654 | 0.9780 | -0.4807 | 541 |

Angles between planes: 1-2, 44.2°; 1-3, 42.0°; 4-5, 41.6°; 4-6, 43.5°.

^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 a^* , y_0 to $c \times a^*$, and z_0 to c .

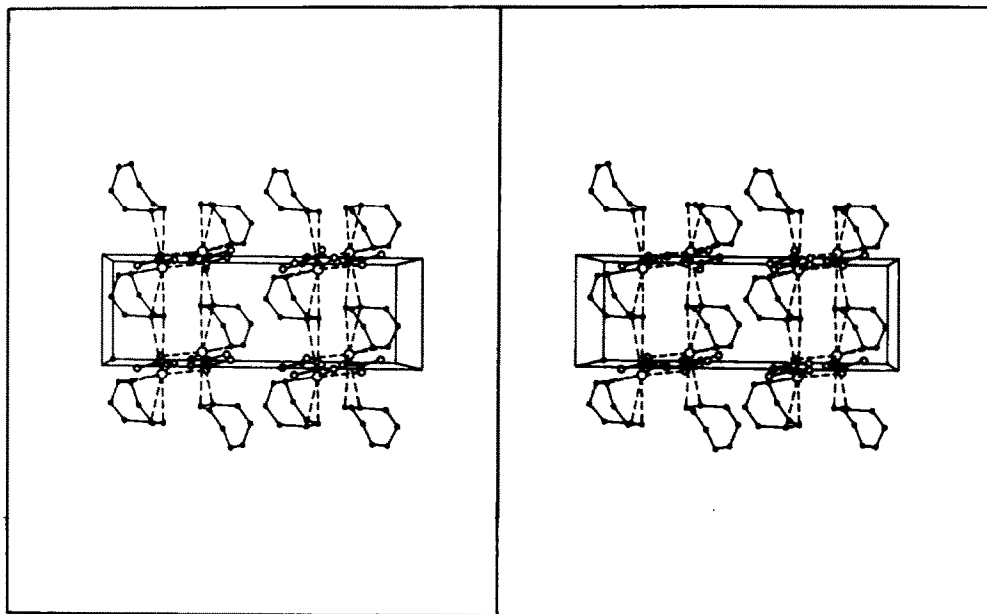


Fig. 2. Stereo drawing showing the packing arrangement, with metal–ligand interactions represented by dotted lines. The unit-cell origin lies at the lower left corner. A left-handed set of axes was used: a points from left to right, b towards the reader, and c upwards.

strongest metal–olefin bond lying in the equatorial plane (Table 4), and the weakest π ligand in an axial position (Fig. 1). The two unequal Ag–O bonds bracket the distance of 2.384 Å observed in crystalline silver nitrate [9].

The D_{2d} tub conformation (bond angle $\theta = 126.1^\circ$; torsion angle about single bond $\omega = 57.9^\circ$ calculated from $\cos\omega = \cotan^2\theta$ [10]; dihedral angle $\delta = 43.2^\circ$ calculated from $\tan^2\delta = \tan^2\theta - 1$) of free COT [11] is slightly distorted as a consequence of coordination to the Ag^{I} ion; this may be seen from the torsion angles listed in Table 3 and the dihedral angles shown in Table 4. The coordinated double bonds at the 1,5-positions (mean = 1.339 Å), which have virtually the same length as the double bond (1.340 Å) in COT, are significantly longer than the uncoordinated ones (mean = 1.308 Å) at the 3,7-positions. The C–C single bonds in the present adduct average to 1.466 Å, in good agreement with the corresponding distance of 1.476 Å in COT.

Strong interaction with the Ag^{I} ion also affects the geometry of the nitrate group. The NO_3^- skeleton remains planar, though two of the three bond angles deviate significantly from 120° . The bond distances vary in the order $\text{N–O}(2) < \text{N–O}(3) < \text{N–O}(1)$, which correlates well with the extent of metal–oxygen interactions in the crystal structure. The present adduct thus differs from most nitrate Ag^{I} complexes, in which the nitrate group is virtually undistorted [8,12,13].

References

- 1 W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Annalen*, 560 (1948) 1.
- 2 A.C. Cope and F.A. Hochstein, *J. Amer. Chem. Soc.*, 72 (1950) 2515.

- 3 F.S. Mathews and W.N. Lipscomb, *J. Amer. Chem. Soc.*, 80 (1958) 4745.
- 4 F.S. Mathews and W.N. Lipscomb, *J. Phys. Chem.*, 63 (1959) 845.
- 5 SHELXTL User Manual, Revision 3, Nicolet XRD Corporation, Cupertino, 1981.
- 6 A. Albinati, S.V. Meille, and G. Carturan, *J. Organometal. Chem.*, 182 (1979) 269.
- 7 O. Ermer, H. Eser, and J.D. Dunitz, *Helv. Chim. Acta*, 54 (1971) 2469, and references therein.
- 8 R.A. Stein and C. Knobler, *Inorg. Chem.*, 16 (1977) 242.
- 9 P. Meyer, A. Rimsky, and R. Chevalier, *Acta Cryst.*, B, 34 (1978) 1457.
- 10 J.D. Dunitz and J.A. Ibers (Eds.), *Perspectives in Structural Chemistry*, Vol. II, Wiley, New York, 1968, p.47.
- 11 M. Traetteberg, *Acta Chem. Scand.*, 20 (1966) 1724.
- 12 D.J. Robinson and C.H.L. Kennard, *J. Chem. Soc.*, B, (1970) 965.
- 13 R.L. Bodner and A.I. Popov, *Inorg. Chem.*, 11 (1972) 1410.