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Notes

Tetramethyl-*cyclo*-tetraarsaoxane, *cyclo*-(CH_3AsO)$_4$: Its Crystal Structure and That of Its Methylcymantrene Complex [Cp′Mn(CO)$_2$]$_2$[*cyclo*-(CH_3AsO)$_4$]

Anthony-J. DiMaio and Arnold L. Rheingold*

Department of Chemistry and Biochemistry and the Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19716

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Summary: The tetrameric arsenic–oxygen heterocycle tetramethyl-*cyclo*-tetraarsaoxane, *cyclo*-(CH_3AsO)$_4$, is obtained as a crystalline single phase from the aerobic oxidation of homocyclic pentamethyl-*cyclo*-pentaarsine, *cyclo*-(CH_3As)$_5$, via a metal–carbonyl template reaction using $Mn_2(CO)_{10}$. A chair-boat ring conformation for this cyclooctane analogue has been determined crystallographically: $C_4H_{12}As_4O_4$, monoclinic, $P2_1/n$, a = 9.229 (3) Å, b = 8.848 (3) Å, c = 14.760 (5) Å, β 95.04 (3)°, V = 1200.6 (7) Å^3, Z = 4, $R(F)$ = 5.28%. The arsaoxane ring readily forms complexes in which two of the four arsenic atoms function as two-electron donors. With methylcymantrene, Cp′Mn(CO)$_3$, [Cp′Mn(CO)$_2$]$_2$[*cyclo*-(CH_3AsO)$_4$] is formed. The eight-membered ring is found crystallographically in a chair conformation, likely for steric reasons: $C_{20}H_{28}As_4Mn_2O_8$, monoclinic, $P2_1/n$, a = 10.842 (2) Å, b = 9.418 (2) Å, c = 14.146 (3) Å, β = 107.49 (2)°, V = 1377.7 (5) Å^3, Z = 4, $R(F)$ = 3.59%.

We recently reported that the heterocyclic, alternating arsenic–oxygen ring systems, methylarsaoxanes,[1] *cyclo*-(CH_3AsO)$_n$ (n = 3 or 4), were attractive oxygen-transfer agents in organometallic oxidations due to their ability to retain "soft", trivalent arsenic ligand properties throughout the oxidation process.[2] Thus, in both reduced and oxidized forms, the potential exists for the performance of stereospecific oxygen-atom transfers. Coordination of the arsenic species and substrate is maintained before, during, and after transfer. In the earlier communication, it was briefly mentioned that the ligand properties of the cyclotetramer, *cyclo*-(CH_3AsO)$_4$ (1), had been demonstrated by the formation of complexes containing intact arsaoxane rings. We wish now to describe this work in more detail and to specifically report the formation and structure of one such complex, [Cp′Mn(CO)$_2$]$_2$[*cyclo*-(CH_3AsO)$_4$] (2) (Cp′ = η^5-$CH_3C_5H_4$), and also that of the uncoordinated cyclotetramer (1).

There are surprisingly few prior reports of complexes of alternating atom, heterocyclic *cyclo*-(REO)$_n$ (E = group 15 element) systems when compared to E–N ring systems. Knowledge of E = P complexes is limited to reports of tri- and tetrameric ring systems serendipitously assembled from (i-Pr_2N)$_2$P(O)H,[3] and the only E = As complex is a cyclohexameric system, [Mo(CO)$_3$]$_2$[*cyclo*-(CH_3AsO)]$_6$, also serendipitously assembled.[4]

Arsaoxanes have been previously prepared by a wide variety of procedures, the most important of which have been the reduction of arsonic acids (usually by sulfur dioxide), the hydrolysis of organoarsenic dihalides, and the oxidation of primary arsines or cyclopolyarsines.[5] These procedures often lead to the complex mixtures of cyclic and linear oligomers; equilibrium compositions for methylarsaoxanes have been studied by NMR methods.[6] Direct contact of air with pentamethyl-*cyclo*-pentaarsine, *cyclo*-(CH_3As)$_5$ (3), is pyrophoric, but in solution, 3 may be slowly oxidized by air to form oligomeric polymethylpolyarsaoxanes. These same oligomers are present at levels of 5–20% in all samples of 3 prepared from aqueous reagents, e.g., the hypophosphorous acid reduction of methylarsonic acid. The arsaoxanes may be identified by the envelope of ^{1}H NMR resonances 0.1–0.3 ppm upfield from 3.[7] (These upfield peaks have been previously incorrectly identified as other oligomers and conformers of 3, and not their oxidation products.)

Pure samples of 3, either prepared from methylarsine and dibenzylmercury[8] or purified by chromatography, thermolytically (170 °C, 48 h) react with $M_2(CO)_{10}$ (M = Mn or Re) in toluene, first to form [Mn(CO)$_4$][μ-(CH_3)$_2$As)]$_2$ (4) and {*cyclo*-[(CH_3As)$_7$As]Mn(CO)$_4$}$Mn_2(CO)_6$ (5).[9,10] If air is admitted to this system during workup (in the first instance inadvertently), a singlet grows rapidly in the ^{1}H NMR spectrum at δ 1.41, indicating the formation of *cyclo*-(CH_3AsO)$_4$. On cooling, crystalline cyclotetramer is obtained in good yield. Under similar conditions, in the absence of metallic coreactants, 15–20 resonances are found in this region, indicating the presence of an oligomeric family of species. The polynuclear metal complex is apparently serving as a template for the formation of single-dimension arsaoxane species.

Photolysis of a mixture of Cp′Mn(CO)$_3$ and the homocycle 3 produces a complex identified spectroscopically as containing an intact five-membered pentaarsenic ring with

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(1) Compounds possessing the empirical formula CH_3AsO have been known by many different names: arsenosomethane, oxymethylarsine, methyloxoarsine, and methylarsine oxide. According to the most modern nomenclature, either methylarsoxane or methylarsaoxane is correct. Preference is given to the latter due to its greater clarity when spoken.

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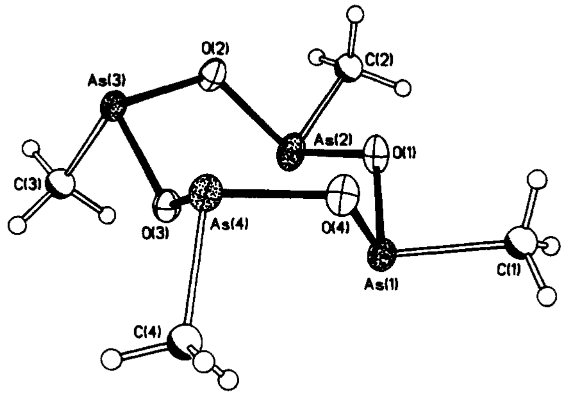

Figure 1. Molecular structure of *cyclo*-$(CH_3AsO)_4$ (1) drawn with 40% probability ellipsoids.

Table I. Crystallographic Data for 1 and 2

	1	2
	(a) Crystal Parameters	
formula	$C_4H_{12}As_4O_4$	$C_{20}H_{26}As_4Mn_2O_8$
fw	423.78	804.04
space group	$P2_1/n$	$P2_1/n$
cryst system	monoclinic	monoclinic
a, Å	9.229 (3)	10.842 (2)
b, Å	8.848 (3)	9.418 (2)
c, Å	14.760 (5)	14.146 (3)
β, deg	95.04 (3)	107.49 (2)
V, Å^3	1200.6 (7)	1377.7 (5)
Z	4	2
cryst dimens, mm	0.21 × 0.21 × 0.36	0.30 × 0.30 × 0.38
cryst color	pale yellow	yellow
D(calc), g/cm^3	2.34	1.94
μ(Mo Kα), cm^{-1}	110.01	56.8
temp, °C	23	23
T(max)/T(min)	2.30	1.56
	(b) Data Collection	
diffractometer	Nicolet R3m	
monochromator	graphite	
scan technique	ω	
radiation	Mo Kα (λ = 0.71073 Å)	
2θ scan range, deg	4–55	4–50
rflns collected	2111	2700
indpt rflns	1884	2424
R(merg), %	5.70	2.90
indpt rflns obsd ($n\sigma(F_o)$)	1175 (n = 5)	1704 (n = 5)
std rflns	3 std/197 rflns	3 std/197 rflns
var in stds, %	<1	<1
	(c) Refinement	
$R(F)$, %	5.28	3.59
$R(wF)$, %	6.02	3.75
Δ/σ(max)	0.008	0.025
$\Delta\rho$, e Å^{-3}	0.94	0.78
N_o/N_v	10.8	10.2
GOF	1.25	1.02

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for 1

	x	y	z	U^a
As(1)	298 (2)	1701 (2)	8598 (1)	44 (1)
As(2)	1725 (2)	1232 (2)	6814 (1)	55 (1)
As(3)	−972 (2)	−742 (2)	6086 (1)	40 (1)
As(4)	−2510 (2)	45 (2)	7810 (1)	47 (1)
O(1)	835 (10)	2447 (11)	7549 (6)	53 (4)
O(2)	247 (10)	803 (12)	5992 (6)	49 (4)
O(3)	−988 (9)	−752 (11)	7318 (6)	42 (3)
O(4)	−1628 (9)	1708 (12)	8301 (6)	53 (4)
C(1)	344 (16)	3641 (19)	9197 (10)	62 (6)
C(2)	2445 (23)	2842 (25)	6123 (11)	113 (10)
C(3)	435 (17)	−2362 (18)	6095 (10)	60 (6)
C(4)	−2308 (19)	−1252 (21)	8864 (10)	78 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for 2

	x	y	z	U^a
As(1)	2123.1 (6)	4068.7 (7)	5751.1 (4)	41.9 (2)
As(2)	472.8 (6)	5342.9 (7)	3743.5 (5)	45.9 (2)
Mn	2810.6 (9)	2252 (1)	4987.0 (7)	42.9 (3)
O(1)	1399 (4)	5584 (4)	5031 (3)	44 (2)
O(2)	858 (4)	3542 (5)	6232 (3)	56 (2)
O(3)	5272 (5)	1912 (7)	6540 (4)	95 (3)
O(4)	3969 (7)	4147 (6)	3863 (5)	98 (3)
C(1)	3206 (7)	5138 (8)	6841 (5)	61 (3)
C(2)	1293 (7)	6857 (9)	3249 (5)	71 (3)
C(3)	4293 (6)	2090 (8)	5927 (5)	59 (3)
C(4)	3521 (7)	3423 (8)	4313 (5)	59 (3)
C(5)	2576 (7)	395 (7)	4089 (5)	57 (3)
C(6)	1547 (7)	1329 (7)	3682 (5)	63 (3)
C(7)	885 (6)	1535 (7)	4383 (5)	58 (3)
C(8)	1495 (7)	706 (7)	5218 (6)	60 (3)
C(9)	2547 (7)	−7 (7)	5028 (5)	56 (3)
C(10)	3392 (14)	−1078 (12)	5712 (10)	87 (5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Bond Distances and Angles for *cyclo*-$(CH_3AsO)_4$ (1)

	(a) Bond Distances, Å		
As(1)–O(1)	1.792 (10)	As(4)–O(3)	1.782 (9)
As(1)–O(4)	1.793 (8)	As(4)–O(4)	1.803 (10)
As(2)–O(1)	1.778 (10)	As(1)–C(1)	1.929 (17)
As(2)–O(2)	1.785 (9)	As(2)–C(2)	1.906 (2)
As(3)–O(2)	1.784 (10)	As(3)–C(3)	1.933 (16)
As(3)–O(3)	1.819 (8)	As(4)–C(4)	1.928 (16)
	(b) Bond Angles, deg		
O(1)–As(1)–O(4)	97.6 (4)	As(1)–O(1)–As(2)	118.8 (6)
O(1)–As(2)–O(2)	100.2 (4)	As(2)–O(2)–As(3)	124.0 (5)
O(2)–As(3)–O(3)	98.2 (4)	As(3)–O(3)–As(4)	118.8 (5)
O(3)–As(4)–O(4)	98.2 (4)	As(4)–O(4)–As(1)	119.9 (6)

Table V. Bond Distances and Angles for $[Cp'Mn(CO)_2]_2$[*cyclo*-$(CH_3AsO)_4$] (2)

	(a) Bond Distances, Å		
CNT–Mn	1.765 (5)	As(1)–O(1)	1.792 (4)
Mn–As(1)	2.266 (1)	As(1)–O(2)	1.775 (5)
Mn–C(3)	1.758 (6)	As(2)–O(1)	1.810 (4)
Mn–C(4)	1.778 (8)	As(2)–O(2)	1.793 (5)
	(b) Bond Angles (deg)		
CNT–Mn–As(1)	122.2 (2)	Mn–As(1)–O(1)	118.7 (1)
CNT–Mn–C(3)	123.4 (4)	Mn–As(1)–O(2)	112.0 (2)
CNT–Mn–C(4)	125.3 (4)	As(1)–O(1)–As(2)	119.2 (2)
As(1)–Mn–C(3)	93.5 (3)	As(1)–O(2)–As(2a)	124.2 (3)
As(1)–Mn–C(4)	92.6 (3)	O(1)–As(1)–O(2)	100.6 (2)
C(3)–Mn–C(4)	90.9 (3)	O(1)–As(2)–O(2a)	96.5 (2)

Table VI. Endocyclic Arsenic–Oxygen Torsional Angles (deg) in *cyclo*-$(CH_3AsO)_4$ (1) and $[Cp'Mn(CO)_2]_2(CH_3AsO)_4$ (2)

1		2	
As(1)–O(1)	−109.6	As(1)–O(1)	−90.1
O(1)–As(2)	101.4	O(1)–As(2)	135.4
As(2)–O(2)	−89.2	As(2)–O(2a)	−79.1
O(2)–As(3)	33.4	O(2a)–As(1a)	17.2
As(3)–O(3)	102.3	As(1a)–O(1a)	90.1
O(3)–As(4)	−109.2	O(1a)–As(2a)	−135.4
As(4)–O(4)	−24.7	As(2a)–O(2)	79.1
O(4)–As(1)	92.5	O(2)–As(1)	−17.2

1,3 coordination of $Cp'Mn(CO)_2$ groups, $[Cp'Mn(CO)_2]_2(CH_3As)_5$ (6). If air is admitted to this reacting system or, if under identical conditions, $Cp'Mn(CO)_3$ is combined directly with 1, 2 is formed in 30–40% yield. The structure of 2 (shown in Figure 1 with metrical data in Table II) contains an intact tetrameric (eight-membered) arsaoxane

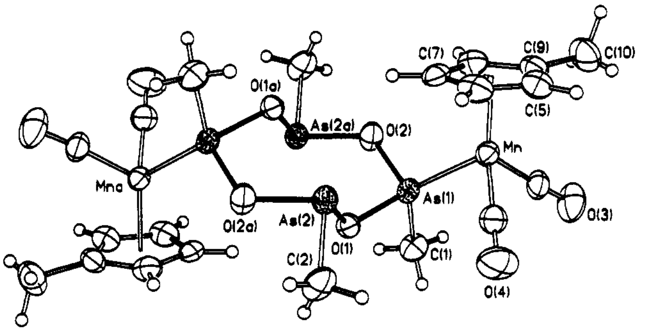

Figure 2. Molecular structure of $[Cp'Mn(CO)_2]_2[(cyclo-(CH_3AsO)_4]$ (**2**) drawn with 40% probability ellipsoids.

ring in a twisted chair conformation with $Cp'Mn(CO)_2$ substitution at the 1 and 5 (head and foot of the chair) ring positions corresponding to As(1) and As(1a). The endocyclic torsion angles given in Table VI show angular distortions of up to 17° from a regular chair conformation; also in an ideal chair, the As(1)–O(1) and As(2)–O(2a) angles would be equal.

Although this ring conformation is not favored for isolobal cyclooctane and is not found in the uncomplexed ring, it appears to be one in which the two $Cp'Mn(CO)_2$ substituents are well separated, at least more so than in the more favored chair–boat or crown conformations.[11] The coordination geometry at Mn is the expected "three-legged" piano stool". The Mn–As(1) distance, 2.266 (1) Å, is short compared to that of $[CpMn(CO)_2][\mu\text{-Ph(H)AsAs(H)Ph}]$ with a 2.319 (2) Å Mn–As bond distance.[12] In fact, although there is no reason to suggest the presence of Mn–As π-bonding in **2**, the distance is identical with that found in $PhAs[CpMn(CO)_2]_2$, in which the phenylarsinidene group is a formal four-electron donor in a planar As-atom environment.[13] In **2**, coordination to the ring is apparently restricted to disubstitution for steric reasons; smaller 16-electron groups may be able to coordinate all 4 As atoms. This proposal is currently being tested.

The parent cyclotetramer **1** (see Figure 2 and Table III) crystallizes in the boat–chair conformation (torsion angles are given in Table VI), which is predicted to be the lowest energy conformation for cyclooctane.[11] In contrast, in the arsathiane analogue, *cyclo*-$(CH_3AsS)_4$, both of the crystallographically independent rings crystallize in the crown conformation.[14] The average As–O distance in **1**, 1.79 (1) Å, is identical with that found in **2**.

Experimental Section

All operations were carried out under dinitrogen, except as noted. Infrared measurements were made on a Nicolet 50XB FTIR spectrophotometer. ^1H NMR spectra were run on a Brucker AM-250 spectrometer and were referenced to TMS. $Cp'Mn(CO)_3$ and $Mn_2(CO)_{10}$ were purchased from Alfa, and *cyclo*-$(CH_3As)_5$ was prepared as described previously.[8] Solvents were dried by standard procedures and degassed prior to use. *CAUTION: Reactions conducted in sealed Carius tubes may produce pressures of up to 50 atm at the reaction temperatures. Tubes should be heated only after enclosure in steel jackets.*

Reaction of $Mn_2(CO)_{10}$ with *cyclo*-$(AsCH_3)_5$. A Carius tube constructed on medium-wall Pyrex tubing was charged with 0.52 g of $Mn_2(CO)_{10}$ (1.33 mmol) and 1.55 g of *cyclo*-$(CH_3As)_5$ in 15 mL of toluene. After degassing, the tube was sealed and heated to 170 °C for 48 h. After cooling slowly to room temperature, the tube was opened, the contents were filtered, and the filtrate was concentrated to a yellow–orange oil. This oil was redissolved in CH_2Cl_2 and chromatographed on alumina. Two major bands were isolated with 1:9 CH_2Cl_2/hexanes. The first band was identified as $Mn_2(CO)_8[\mu\text{-}(CH_3)_2As]_2$: ^1H NMR ($CDCl_3$) δ 1.87 (singlet). IR ($CDCl_3$) ν_{CO} 2048 (s), 1996 (s), 1957 (s). The second band was identified as $\{cyclo\text{-}[(AsCH_3)_7As]Mn(CO)_4\}Mn_2(CO)_6$ (**5**) by a ^1H NMR pattern similar to that for the previously reported Re analogue:[10] ^1H NMR ($CDCl_3$) δ 2.30, 2.28, 2.12, 2.04, 2.01, 1.85, 1.12, 1.09 (all 3 H singlets). During a prolonged effort to obtain diffraction-grade crystals of **5**, the sample was unintentionally exposed to air. This led to the slow formation of a pale yellow crystalline product that precipitated from solution in 42% yield. It was identified crystallographically as **1**. ^1H NMR ($CDCl_3$) δ 1.51. No other NMR-detectable arsaoxane species were present in solution. Crystalline samples of **1** may be more directly obtained by previously disclosed procedures.[6b]

Photolysis of $Cp'Mn(CO)_3$ and *cyclo*-$(CH_3As)_5$. A quartz tube was fitted with a micro-Schlenk apparatus (Ace Glass), stir bar, and cold finger condenser and flushed with N_2. To this apparatus, 6 mL of $Cp'Mn(CO)_3$ (44 mmol) and 20 mL of a 4.8% (by weight) solution of **3** in toluene were added. The mixture was irradiated at room temperature for 4 h with a low-pressure mercury lamp. The solution was evaporated, and the fraction of the residue soluble in toluene was chromatographed on alumina with 5% toluene in hexanes. This afforded a single red product identified as 1,3-$[Cp'Mn(CO)_2]_2[\mu\text{-}cyclo\text{-}(CH_3As)_5]$ (**6**). IR ($CHCl_3$) ν_{CO} 1993 (s), 1945 (s), 1905 (s), 1859 (s). ^1H NMR ($CDCl_3$) gave three slightly broadened peaks in a 4:3:1 integration ratio: δ 4.53, 1.91, 1.60. If air is admitted to red solutions of **6**, the ^1H NMR spectrum gradually changes until **6** is consumed and a new red species is formed, which was identified as **2**. The solid residue obtained following evaporation of solvent was recrystallized from toluene by vapor diffusion of pentane. The isolated yield of **2** from **6** was about 50%. ^1H NMR ($CDCl_3$) δ 4.51 (4 H), 4.36 (4 H), 1.80 (6 H), 1.62 (12 H). Mp 168–170 °C (dec).

Crystal Structure Determinations. Crystallographic data are collected in Table I. Samples of both **1** and **2** (both grown from toluene) were mounted in capillary tubes and found from photographic evidence and diffraction symmetry to belong to the $2/m$ Laue group. Systematic absences in the data uniquely defined the monoclinic space group $P2_1/n$. Empirical corrections for absorption were applied to the data by using a pseudoellipsoid model.

Both structures were solved by direct methods. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed in idealized locations. All calculations used SHELXTL software (G. Sheldrick, Nicolet (Siemens) XRD, Madison, WI). Atomic coordinates for **1** and **2** are given in Tables II and III, and bond distances and angles are given in Tables IV and V. Ring torsion angles are given in Table VI.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, partially funded this research.

Registry No. 1, 53632-03-4; **2**, 136144-68-8; **3**, 20550-47-4; **4**, 21328-87-0; **5**, 136115-29-2; **6**, 136144-69-9; $Mn_2(CO)_{10}$, 10170-69-1; $Cp'Mn(CO)_3$, 12108-13-3.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1** and **2** (4 pages); tables of structure factors for **1** and **2** (21 pages). Ordering information is given on any current masthead page.

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