Synthesis and Structure of Tetraethylcyclotetraarsathiane and its Complexes $[Ag\{cyclo\text{-}(C_2H_5AsS)_4\}_2]CF_3SO_3$ and $[cyclo\text{-}(C_2H_5AsS)_4]\cdot 2SbBr_3$

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Ethylcyclotetraarsathiane, Silver (I) Complex, Crystal Structure

Ethylcycloarsathiane $(C_2H_5AsS)_n$ crystallizes as a crown-shaped cyclotetramer **1** from a chloroform/pyridine solution. ^1H and ^{13}C NMR studies indicate the presence of two major oligomers in $CHCl_3$ solution in an approximately 1:1 ratio. Reaction of **1** with $AgCF_3SO_3$ yields $[Ag\{cyclo\text{-}(C_2H_5AsS)_4\}_2]CF_3SO_3$ (**2**) in which the silver(I) cation exhibits a distorted quadratic-antiprismatic coordination geometry with four shorter (2.716(7), 2.767(5) Å) and four longer (3.218(6), 3.328(9) Å) Ag–S distances. The tetraethylcyclotetraarsathiane ligand exhibits a K^1S coordination mode in the complex $[cyclo\text{-}(C_2H_5AsS)_4]\cdot 2SbBr_3$ (**3**) with the sulphur atom adopting an axial positon in a ψ-trigonal bipyramidal antimony coordination polyhedron.

Introduction

Our studies on the coordination properties of ethylcycloarsoxane $(C_2H_5AsO)_n$, $n = 4$–6 [1–3], have demonstrated that such ambidentate macrocycles are capable of acting as ionophores for alkali metal cations in a manner similar to classical crown ethers [2]. These findings prompted us to investigate the complexing ability of ethylcycloarsathiane $(C_2H_5AsS)_n$, which may be compared with macrocyclic thioethers. The current interest in the coordination chemistry of crown thioethers such as $[9]aneS_3$ (1,4,7-trithiacyclononane), $[12]aneS_3$, $[14]aneS_4$ and $[18]aneS_6$ is witnessed by recent review articles [4, 5]. Most attention has focused on the ability of such macrocyclic ligands to bind transition-metal ions, particularly those in lower oxidation states, which may be regarded as "soft" Lewis-acids. In contrast, a mere handful of main-group complexes have been synthesized and structurally characterized. These include a number of SbX_3 (X = Cl, I) [6, 7] and $BiCl_3$ adducts [6, 8, 9].

Although the synthesis of alkylarsathianes $(RAsS)_n$ by the reaction of $RAsCl_2$ with H_2S was reported in the previous century [10] it is only relatively recently that isolated examples have been structurally characterized. The tetramers $(CH_3AsS)_4$ [11], $(t\text{-}BuAsS)_4$ [12] and $(PhAsS)_4$ [13] all exhibit a crown structure in which the central eight-membered ring displays approximately C_{4v} symmetry. Reaction of $(CH_3As)_5$ with S_8 in the presence of $Mo(CO)_6$ in a Carius tube at 125 °C leads to the formation of a mixture of $(CH_3AsS)_3$ and $(CH_3AsS)_4$, which could be successfully separated by column chromatography [11]. As expected the alternating As-S six-membered ring in the trimer $(CH_3AsS)_3$ adopts the chair conformation of cyclohexane. Ethylcycloarsathiane was first prepared as a yellow oil by Kretov and Berlin in 1931 [14], who employed the reaction of $C_2H_5AsCl_2$ with H_2S and described the product as a hexamer on a basis of the molecular weight determination.

To our knowledge no metal complexes of alkyl- or arylcycloarsathianes have previously been described. We now report the crystal structure of the tetramer $cyclo\text{-}(C_2H_5AsS)_4$ **1** and its complexes $[Ag\{cyclo\text{-}(C_2H_5AsS)_4\}_2]CF_3SO_3$ **2** and $[cyclo\text{-}(C_2H_5AsS)_4]\cdot 2SbBr_3$ **3**.

Experimental

IR spectra were recorded as KBr discs on Perkin-Elmer spectrometers 1700 and 1760, EI-MS (70 eV) on a Finnigan MAT CH-5 and FAB-MS on a Fisons VG Autospec. ^1H and ^{13}C NMR spectra were registered on a Bruker AM 400 with δ values given in ppm. Elemental analyses were performed with a Carlo Erba 1106. All reactions were

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carried out under argon. $(C_2H_5AsO)_n$ was prepared by the alkaline hydrolysis (K_2CO_3) of $C_2H_5AsBr_2$ in benzene solution [15]. As described below *cyclo*-$(C_2H_5AsS)_4$ was prepared by the novel reaction of $(C_2H_5AsO)_n$ with H_2S. A similar strategy was previously employed by Schulte [16] for the preparation of $(PhAsS)_4$.

$(C_2H_5AsS)_4$ **1**

H_2S was passed through a solution of 10 g $(C_2H_5AsO)_n$ in 20 ml ethanol for 45 min. Removal of ethanol left $(C_2H_5AsS)_n$ as a viscous oil, which was redissolved in 30 ml $CHCl_3$ and dried over $CaCl_2$. Filtration and removal of $CHCl_3$ afforded $(C_2H_5AsS)_n$ as a highly viscous colourless oil in effectively quantitative yield. 420 mg of the product was dissolved in 5 ml $CHCl_3$ in the presence of 0.5 ml pyridine. The solution was covered with diethyl ether and left to stand at −40 °C to afford colourless crystals of $(C_2H_5AsS)_4$ (**1**) over a period of 4 d (yield 59%).

$C_8H_{20}S_4As_4$ (**1**), *M = 544.2*
Calcd C 17.7 H 3.7%,
Found C 17.5 H 3.6%.

FAB-MS: *m/z* (%) 680 (2) $[Et_5As_5S_5]^+$, 651 (12) $[Et_4As_5S_5]^+$, 544 (14) $[Et_4As_4S_4]^+$, 515 (74) $[Et_3As_4S_4]^+$, 408 (78) $[Et_3As_3S_3]^+$, 379 (42) $[Et_2As_3S_3]^+$, 272 (31) $[Et_2As_2S_2]^+$, 243 (100) $[EtAs_2S_2]^+$. – ^1H NMR ($CDCl_3$) 1.35, 1.39 (2 t, 12 H, CH_3), 2.22, 2.37 (2 q, 8 H, CH_2). – ^{13}C NMR ($CDCl_3$) 10.52, 10.94 (CH_3), 29.43, 29.97 (CH_2). – IR (cm^{-1}) 2952 s, 2917 s, 2862 m, 2725 w, 1451 vs, 1405 m, 1373 s, 1262 m, 1207 s, 1099 m, 1022 vs, 958 m, 803 m, 722 m, 559 s, 398 s, 385 s, 370 vs, 287 w.

[Ag{cyclo-$(C_2H_5AsS)_4\}_2]CF_3SO_3$ (**2**)

83 mg (0.32 mmol) $AgCF_3SO_3$ was added to a solution of 352 mg (2.58 mmol for *n* = 1) of $(C_2H_5AsS)_n$ in 7 ml $CHCl_3$. After stirring for 1 h the solution was covered with diethyl ether and left to stand at room temperature to yield colourless crystals of **2** over a period of 3 d (yield 78%).

$C_{17}H_{40}O_3F_3S_9As_8Ag$ (**2**), *M = 1345.3*
Calcd C 15.2 H 3.0%,
Found C 15.0 H 2.8%.

FAB-MS: *m/z* (%) 1196 (61) $[M^+]$, 1060 (9) $[M-C_2H_5AsS]^+$, 924 (4) $[M-2\,C_2H_5AsS]^+$, 789 (10) $[M-3\,C_2H_5AsS]^+$, 653 (100) $[M-4\,C_2H_5AsS]^+$. – ^1H NMR ($CDCl_3$) 1.40, (t, 24 H, CH_3), 2.41 (q, 16 H, CH_2). – ^{13}C NMR ($CDCl_3$) 10.63 (CH_3), 30.67 (CH_2). – IR (cm^{-1}) 2954 m, 2920 m, 2863 m, 1448 m, 1406 w, 1375 m, 1252 vs, 1221 s, 1153 s, 1026 vs, 971 w, 720 m, 654 m, 635 s, 554 m, 517 m, 400 sh, 375 s, 345 sh, 283 w.

[cyclo-$(C_2H_5AsS)_4] \cdot 2\,SbBr_3$ (**3**)

376 mg (2.76 mmol for *n* = 1) $(C_2H_5AsS)_n$ and 333 mg (0.92 mmol) $SbBr_3$ were dissolved in 20 ml 1:1 $CHCl_3/CH_3CN$. A white precipitate which formed after *ca.* 5 min was filtered off after 1 h and the solution left to stand at −40 °C to yield crystals of **3.**

$C_8H_{20}As_4S_4Sb_2Br_6$ (**3**) *M = 1267.1*
Calcd C 7.6 H 1.6%,
Found C 7.5 H 1.5%.

X-ray structural analyses of **1–3**

Table I contains crystal and refinement data for **1–3.** Unit cell constants were obtained from least-squares fits to the settings for 25 reflections centered on a Siemens P4 diffractometer. Intensity data were collected on the diffractometer with varied scan rates (1.8–15.0° min^{-1}, ω-scan) using MoK_α radiation (λ = 0.71073 Å) at room temperature (295 K) for **1** and **3** and at 173 K for **2.** The lower measurement temperature was necessary for the latter structure in order to reduce the thermal parameters of the anionic F and O atoms. Three selected reflections were monitored every 100 reflections during the course of data collection; significant deviations in intensity were not observed. Semi-empirical absorption corrections were performed on the basis of ψ scans for **1** (μ = 76.3 cm^{-1}, min./max. transmission 0.0034/0.0173) and **3** (μ = 147.8 cm^{-1}, min./max. transmission 0.0210/0.0701). The $|F_o|$ values for **2** were corrected using DIFABS [17]. Structure solution and refinement were performed with the SHELXTL program system (Siemens). Crystallographic C_2 symmetry is observed for the cation [Ag{*cyclo*-$(C_2H_5AsS)_4\}_2]^+$ in **2** with the $CF_3SO_3^-$ anion occupying disordered positions (site occupation factors = 0.5) similarly related by a twofold rotation axis. Anisotropic temperature factors were introduced for all non-hydrogen atoms in **1.** This was likewise the case in **2** and **3** with the exception of the disordered anionic F, O and C atoms in the former and the cycloarsathiane C atoms in the latter structure. Hydrogen atoms in **1** were assigned group isotropic temperature factors for the methylene and methyl functions and their positions calculated geometrically. The assignment of the absolute structure of **2** (space group $P3_121$)

Table I. Crystal and Refinement data for **1–3**.

Compound	**1**	**2**	**3**
Space group	$P2_1/n$	$P3_121$	$P\bar{1}$
Meas. temperature (K)	295	173	295
a (Å)	9.785(2)	10.488(2)	9.727(2)
b (Å)	15.770(4)	10.488(2)	12.229(2)
c (Å)	12.034(3)	32.479(7)	12.633(3)
α (°)	90	90	79.93(3)
β (°)	99.00(2)	90	80.54(3)
γ (°)	90	120	86.68(3)
V (Å^3)	1834.1(8)	3042(1)	1458.8(5)
Z	4	3	2
F (000)	1056	1944	1152
M	544.2	1345.3	1267.1
D_{calc} (g·cm^{-3})	1.97	2.20	2.88
crystal size (mm)	0.52×0.50×0.41	0.52×0.44×0.42	0.52×0.46×0.30
radiation	MoK_α	MoK_α	MoK_α
μ (cm^{-1})	76.3	74.7	147.8
scan range (°)	$2\theta \leq 50°$	$2\theta \leq 55°$	$2\theta \leq 45°$
scan type	ω	ω	ω
reflections collected	3562	2947	3808
independent reflections	3224	2751	3777
observed reflections	2176	1799	2590
rejection criterion	$F_o^2 \leq 1.5\,\sigma(F_o^2)$	$F_o^2 \leq 2\,\sigma(F_o^2)$	$F_o^2 \leq 2\,\sigma(F_o^2)$
absorption correction	ψ-scans	DIFABS	ψ-scans
R	0.056	0.065	0.056
R_w	0.051	0.062	0.053
S (goodness-of-fit)	1.90	2.33	2.09
g	0.0001	0.0001	0.0001
min./max. res. (e·Å^{-3})	−0.48/0.93	−1.06/1.12	−1.24/1.42

Tab. II. Atom coordinates (×10^4) with equivalent isotropic temperature factors (Å^2×10^3) for **1–3**.

Atom	x/a	y/b	z/c	U_{eq}*
Compound **1**				
As(1)	2159(1)	1268(1)	1239(1)	69(1)
As(2)	895(1)	3095(1)	122(1)	70(1)
As(3)	−2283(1)	2236(1)	−106(1)	71(1)
As(4)	−1039(1)	417(1)	1081(1)	66(1)
S(1)	2167(3)	2640(2)	1737(3)	80(1)
S(2)	−1162(3)	3405(2)	627(3)	87(1)
S(3)	−2472(3)	1463(2)	1435(3)	78(1)
S(4)	840(3)	645(2)	2373(3)	76(1)
C(11)	3909(11)	955(8)	2169(11)	85(5)
C(12)	4285(14)	41(8)	1908(13)	107(7)
C(21)	1592(11)	4258(7)	191(11)	84(5)
C(22)	3061(11)	4299(8)	−93(11)	85(5)
C(31)	−4134(10)	2721(8)	−250(10)	79(5)
C(32)	−5234(12)	2106(9)	−804(12)	95(6)
C(41)	−1844(12)	−459(7)	1945(11)	83(5)
C(42)	−940(14)	−1247(7)	2151(11)	93(6)

Tab. II (continued).

Atom	x/a	y/b	z/c	U_{eq}*
Compound **2**				
Ag(1)	605(3)	0	8333	42(1)
As(1)	4376(2)	2806(2)	8810(1)	42(1)
As(2)	1466(3)	3030(2)	9146(1)	43(1)
As(3)	509(3)	3658(2)	8215(1)	45(1)
As(4)	3581(3)	3626(3)	7865(1)	53(1)
S(1)	2090(6)	1272(6)	9057(2)	48(3)
S(2)	−574(7)	2122(7)	8751(2)	69(3)
S(3)	1081(7)	2255(7)	7826(2)	67(3)
S(4)	4081(7)	1975(6)	8156(2)	53(3)
C(11)	5314(26)	1646(26)	8972(6)	63(15)
C(12)	5484(37)	1574(35)	9421(6)	99(22)
C(21)	387(24)	2213(25)	9669(5)	68(15)
C(22)	−868(30)	656(27)	9659(8)	98(10)
C(31)	−1364(20)	3172(20)	7936(5)	45(11)
C(32)	−2410(22)	1570(22)	7843(6)	51(12)
C(41)	3829(33)	3235(33)	7284(6)	107(10)
C(421)	5060(48)	2963(60)	7204(12)	89(18)
C(422)	3729(58)	4486(45)	7050(10)	76(15)
S	4771(8)	4771(8)	10000	68(4)
O(1)	3421(30)	3940(38)	10241(11)	217(17)
O(2)	5988(35)	4830(47)	10230(12)	217(17)
O(3)	4677(46)	4346(40)	9581(6)	217(17)
C(1)	5112(34)	6617(20)	10005(9)	231(14)
F(1)	5132(54)	7083(37)	10383(8)	231(14)
F(2)	4078(40)	6756(38)	9801(13)	231(14)
F(3)	6355(36)	7510(31)	9812(12)	231(14)

was based on the successful refinement of the Rogers's η factor to 1.16 (9) [18]. The reliability index R_w is defined as $[\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$ with weights given by $w = [\sigma^2(F_o) + g F_o^2]^{-1}$. Atom coordinates with equivalent isotropic temperature factors are listed in Table II, selected bond lengths

Tab. II (continued).

Atom	*x/a*	*y/b*	*z/c*	U_{eq}*
Compound **3**				
Sb(1)	−443(1)	5918(1)	1681(1)	33(1)
Sb(2)	310(2)	7938(1)	−1843(1)	43(1)
Br(1)	1447(2)	5956(2)	−83(2)	46(1)
Br(2)	588(2)	7607(2)	2074(2)	45(1)
Br(3)	1106(2)	4457(2)	2646(2)	51(1)
Br(4)	−743(3)	9310(3)	−3243(2)	69(1)
Br(5)	−1762(2)	7883(2)	−365(2)	58(1)
Br(6)	1641(3)	9330(3)	−1241(3)	90(1)
As(1)	−5103(2)	4287(2)	2635(2)	30(1)
As(2)	−3083(2)	4335(2)	4599(2)	28(1)
As(3)	−3428(2)	7149(2)	4152(2)	33(1)
As(4)	−5405(2)	7052(2)	2179(2)	31(1)
S(1)	−2935(5)	3766(5)	2986(4)	35(2)
S(2)	−1694(5)	5836(5)	4112(4)	34(2)
S(3)	−3389(6)	7763(5)	2370(4)	44(2)
S(4)	−4640(6)	5688(5)	1245(5)	46(2)
C(11)	−5219(19)	3159(18)	1724(15)	35(5)
C(12)	−5570(24)	2070(22)	2471(20)	64(7)
C(21)	−1607(20)	3302(18)	5128(16)	41(6)
C(22)	−2083(22)	2116(20)	5353(18)	52(7)
C(31)	−2282(21)	8336(19)	4414(17)	47(6)
C(32)	−3197(26)	9392(23)	4513(20)	69(8)
C(41)	−5678(20)	8151(18)	868(16)	39(6)
C(42)	−6099(21)	9306(20)	1221(17)	49(6)

* Equivalent isotropic temperature factors U_{eq} are defined as one third of the trace of the orthogonalized U_{ij} tensor.

Tab. III. Bond lengths (Å) in **1–3**.

Compound **1**			
As(1)–S(1)	2.245(3)	As(1)–S(4)	2.246(4)
As(2)–S(1)	2.254(3)	As(2)–S(2)	2.246(4)
As(3)–S(2)	2.253(3)	As(3)–S(3)	2.250(4)
As(4)–S(3)	2.248(4)	As(4)–S(4)	2.244(3)
As(1)–C(11)	1.96(1)	As(2)–C(21)	1.95(1)
As(3)–C(31)	1.95(1)	As(4)–C(41)	1.97(1)
Compound **2**			
As(1)–S(1)	2.264(5)	As(1)–S(4)	2.257(5)
As(2)–S(1)	2.262(8)	As(2)–S(2)	2.258(7)
As(3)–S(2)	2.254(6)	As(3)–S(3)	2.237(8)
As(4)–S(3)	2.278(7)	As(4)–S(4)	2.252(8)
As(1)–C(11)	1.98(3)	As(2)–C(21)	1.98(2)
As(3)–C(31)	1.98(2)	As(4)–C(41)	1.97(2)
Ag(1)–S(1)	2.767(5)	Ag(1)–S(3)	2.716(7)
Ag(1)–S(2)	3.328(9)	Ag(1)–S(4)	3.218(6)
Compound **3**			
As(1)–S(1)	2.259(5)	As(1)–S(4)	2.236(6)
As(2)–S(1)	2.246(6)	As(2)–S(2)	2.278(6)
As(3)–S(2)	2.261(5)	As(3)–S(3)	2.240(6)
As(4)–S(3)	2.256(6)	As(4)–S(4)	2.333(7)
As(1)–C(11)	1.96(2)	As(2)–C(21)	1.98(2)
As(3)–C(31)	1.98(2)	As(4)–C(41)	1.99(2)
Sb(1)–S(2)	3.099(5)	Sb(1)–Br(1)	2.641(2)
Sb(1)–Br(2)	2.506(3)	Sb(1)–Br(3)	2.546(3)
Sb(1)–Br(1a)	3.578(3)	Sb(1)–Br(5)	3.558(3)
Sb(2)–Br(1)	3.265(3)	Sb(2)–Br(4)	2.520(3)
Sb(2)–Br(5)	2.507(3)	Sb(2)–Br(6)	2.486(4)
Sb(2)–S(1a)	3.490(5)		

Tab. IV. Selected bond angles (°) in **1–3**.

Compound **1**			
S(1)–As(1)–S(4)	103.8(1)	S(1)–As(2)–S(2)	103.5(1)
S(2)–As(3)–S(3)	102.6(1)	S(3)–As(4)–S(4)	102.7(1)
As(1)–S(1)–As(2)	95.6(1)	As(2)–S(2)–As(3)	96.8(1)
As(3)–S(3)–As(4)	96.2(1)	As(1)–S(4)–As(4)	97.8(1)
S(1)–As(1)–C(11)	97.2(4)	S(4)–As(1)–C(11)	94.4(4)
S(1)–As(2)–C(21)	96.9(4)	S(2)–As(2)–C(21)	96.1(3)
S(2)–As(3)–C(31)	95.9(4)	S(3)–As(3)–C(31)	95.2(4)
S(3)–As(4)–C(41)	95.9(4)	S(4)–As(4)–C(41)	95.7(3)
Compound **2**			
S(1)–As(1)–S(4)	99.6(2)	S(1)–As(2)–S(2)	100.5(3)
S(2)–As(3)–S(3)	99.8(3)	S(3)–As(4)–S(4)	100.1(3)
As(1)–S(1)–As(2)	95.8(2)	As(2)–S(2)–As(3)	96.0(2)
As(3)–S(3)–As(4)	99.0(2)	As(1)–S(4)–As(4)	97.9(3)
S(1)–As(1)–C(11)	98.3(6)	S(4)–As(1)–C(11)	91.6(6)
S(1)–As(2)–C(21)	95.3(9)	S(2)–As(2)–C(21)	95.1(6)
S(2)–As(3)–C(31)	95.0(5)	S(3)–As(3)–C(31)	97.5(7)
S(3)–As(4)–C(41)	92.6(9)	S(4)–As(4)–C(41)	97.8(12)
S(1)–Ag(1)–S(2)	68.8(2)	S(1)–Ag(1)–S(3)	106.3(2)
S(2)–Ag(1)–S(3)	68.4(2)	S(2)–Ag(1)–S(4)	108.8(2)
S(3)–Ag(1)–S(4)	71.1(2)	S(1)–Ag(1)–S(1a)	142.5(3)
S(1)–Ag(1)–S(4)	70.0(2)	S(2)–Ag(1)–S(1a)	144.6(2)
S(3)–Ag(1)–S(1a)	83.2(2)	S(4)–Ag(1)–S(1a)	79.6(2)
S(2)–Ag(1)–S(2a)	90.2(2)	S(2)–Ag(1)–S(3a)	90.7(2)
S(2)–Ag(1)–S(4a)	145.3(1)	S(3)–Ag(1)–S(3a)	150.8(3)
S(3)–Ag(1)–S(4a)	137.2(2)	S(4)–Ag(1)–S(4a)	71.7(2)
Compound **3**			
S(1)–As(1)–S(4)	101.1(2)	S(1)–As(2)–S(2)	100.3(2)
S(1)–As(3)–S(3)	100.9(2)	S(3)–As(4)–S(4)	101.8(2)
As(1)–S(1)–As(2)	98.7(2)	As(2)–S(2)–As(3)	96.8(2)
As(3)–S(3)–As(4)	98.7(2)	As(1)–S(4)–As(4)	96.5(2)
S(1)–As(1)–C(11)	95.4(6)	S(4)–As(1)–C(11)	95.4(6)
S(1)–As(2)–C(21)	95.7(7)	S(2)–As(2)–C(21)	94.9(6)
S(2)–As(3)–C(31)	95.8(6)	S(3)–As(3)–C(31)	96.5(6)
S(3)–As(4)–C(41)	94.5(6)	S(4)–As(4)–C(41)	94.5(7)
S(2)–Sb(1)–Br(1)	159.4(1)	S(2)–Sb(1)–Br(2)	79.2(1)
S(2)–Sb(1)–Br(3)	77.2(1)	Br(1)–Sb(1)–Br(2)	89.7(1)
Br(1)–Sb(1)–Br(3)	87.4(1)	Br(2)–Sb(1)–Br(3)	98.0(1)
Br(4)–Sb(2)–Br(5)	96.4(1)	Br(4)–Sb(2)–Br(6)	95.5(1)
Br(5)–Sb(2)–Br(6)	97.5(1)	S(1a)–Sb(2)–Br(4)	113.2(1)
S(1a)–Sb(2)–Br(5)	141.7(1)	S(1a)–Sb(2)–Br(6)	102.9(1)

and angles in Tables III and IV. Further details of the crystal structure analyses may be obtained from Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen upon specification of the deposition number CSD 58229, the authors and the journal.

Discussion

Ethylcycloarsathiane $(C_2H_5AsS)_n$ (**1**) crystallizes as a cyclotetramer from a chloroform/pyridine solution at −40 °C. As may be seen from Fig. 1 the central eight-membered As_4S_4 ring adopts a crown conformation with equatorially sited ethyl groups. Similar conformations are exhibited by the previously characterized cyclotetramers $(CH_3AsS)_4$ [11], $(t\text{-}BuAsS)_4$ [12] and $(PhAsS)_4$ [13]. The As atoms in **1** are displaced ± 0.022 Å,

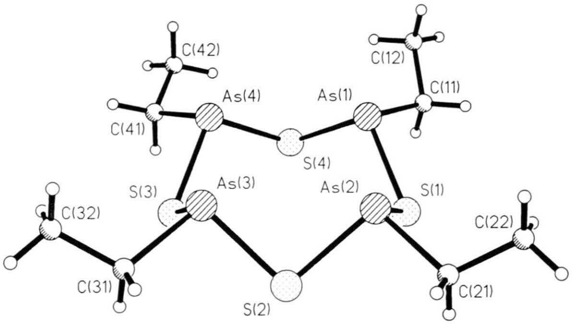

Fig. 1. Molecular structure *cyclo*-$(C_2H_5AsS)_4$ (**1**).

the S atoms ± 0.055 Å from their respective best least-squares planes. Average endocyclic bond lengths and angles of 2.248 (4) Å (As–S), 103.2 (6)° (S–As–S) and 96.6 (9)° (As–S–As) are similar to those in the above cyclotetramers. The ^1H NMR spectrum of ethylcycloarsathiane $(CDCl_3)$ exhibits two major sets of signals for the CH_2 and CH_3 protons with an integrated ratio of approximately 1:1. In view of the observation of significant concentrations of both $(CH_3AsS)_3$ and $(CH_3AsS)_4$ in a CH_2Cl_2 solution of methylcycloarsathiane [11] it may reasonably be assumed that the above ^1H NMR resonances may be assigned to $(C_2H_5AsS)_3$ and $(C_2H_5AsS)_4$. A further three minor sets of triplets (CH_3) and quartets (CH_2) in the respective ranges 1.33–1.39 and 2.24–2.38 ppm with integral values of less than 5% are observed in the ^1H NMR spectrum of $(C_2H_5AsS)_n$, indicating the presence of further oligomers of differing ring size and/or conformation in solution. In this context, it is interesting to note the presence of the cyclopentamer $(C_2H_5AsS)_5$, albeit with a low intensity (2%), in the FAB MS of **1**. In contrast, only fragments based on $n = 1-3$ are registered in the EI MS of ethylcycloarsathiane at an ionization voltage of 70 eV.

As we have previously reported $(C_2H_5AsO)_n$ is an ionophore for alkali metal cations with adaptable ring size [2]. Reaction of $(C_2H_5AsO)_n$ with MSCN (M = Na, K) in CH_3CN leads to formation of respectively [Na{*cyclo*-$(C_2H_5AsO)_4\}_2]$ SCN and [K{*cyclo*-$(C_2H_5AsO)_5\}_2]$ SCN in which the cations exhibit quadratic-antiprismatic and pentagonal-antiprismatic coordination geometries. As the cyclotrimer $(C_2H_5AsO)_3$ predominates in solution [15] it is apparent that metal mediation must be required for the ring expansion to $n = 4$ and 5 in the above Na^+ and K^+ complexes. This finding prompted us to investigate whether a similar phenomenon may be observed for the analogous ethylcycloarsathiane, which also exhibits dynamic reorganization equilibria between ring systems of various size (*e. g.* $n = 3$ and 4), as indicated by the NMR studies discussed above. We chose to study the coordination properties of $(C_2H_5AsS)_n$ towards Ag (I) and Sb (III) (in $SbBr_3$), both of which might be expected to strive towards a coordination number between 4 and 6 when coordinated by cycloarsathiane sulphur atoms [6, 7, 19].

The reaction of $(C_2H_5AsS)_n$ with $AgCF_3SO_3$ in $CHCl_3$ leads to the formation of [Ag{*cyclo*-$(C_2H_5AsS)_4\}_2]CF_3SO_3$ (**2**). As depicted in Fig. 2 the silver cation in **2** displays a remarkable quadratic-antiprismatic coordination in marked contrast to the ubiquity of linear or tetrahedral geometries in Ag (I) complexes. Examples of both two- and four-coordination are known for thioether complexes [19–21]. However, some macrocyclic ligands are able to enforce five- or six-coordination on the d^{10} Ag (I) cation, which displays only weak stereochemical preferences. For instance the trithiane complexes $[Ag_2(1,3,5\text{-trithiane})_5]^{2+}$ [22] and [Ag(1,3,5-trithiane)}X (X = NO_3, ClO_4) [23] exhibit both four- and five-coordinated Ag (I) with Ag–S distances ranging between 2.519 (3) and 2.924 (3) Å. The structures adopted by [9]aneS_3 and [12]aneS_3 complexes are

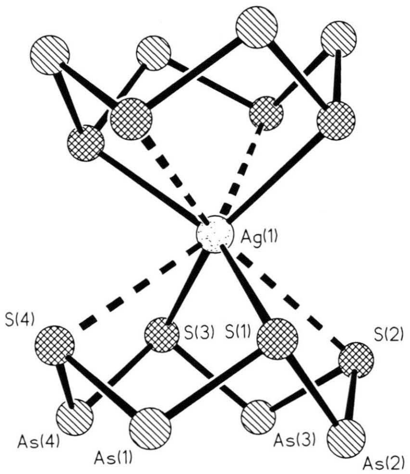

Fig. 2. Side view of the cation [Ag{*cyclo*-$(C_2H_5AsS)_4\}_2]^+$ (**2**). Ethyl groups have been omitted for clarity.

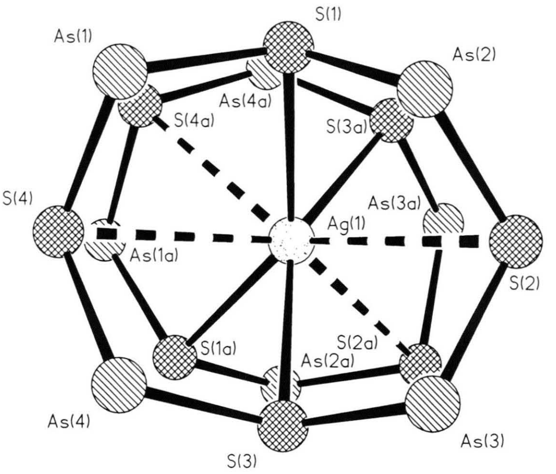

Fig. 3. View of the cation $[Ag\{cyclo\text{-}(C_2H_5AsS)_4\}_2]^+$ (**2**) perpendicular to the planes of the arsathiane rings. Ethyl groups have been omitted for clarity.

instructive [19]. Whereas $[Ag([9]aneS_3)_2]^+$ exhibits a trigonally elongated octahedral geometry with Ag–S distances between 2.696(2) and 2.753(1) and average chelating S–Ag–S angles of 80°, $[Ag([12]aneS_3)]CF_3SO_3 \cdot CH_3CN$ adopts a polymeric network structure in which the Ag (I) cations are coordinated to three thioether sulphur atoms of symmetry related $[12]aneS_3$ molecules. These findings suggest that macrocyclic ligands may be able to enforce a high coordination number on Ag (I) in cases in which ligand and cation display a good size fit for a particular geometry, *e.g.* sixfold coordination in $[Ag([9]aneS_3)_2]^+$. Where this is not the case, polymeric complexes with a typical coordination number of four may be expected. The adoption of six-coordination in a hypothetical triethylcyclotriarsathiane complex $[Ag\{cyclo\text{-}(C_2H_5AsS)_3\}_2]^+$ would, presumably, lead to a very elongated octahedral geometry with unreasonably small chelating S–As–S angles. In contrast, as depicted in Figs. 2 and 3, the cyclotetramer $(C_2H_5AsS)_4$ provides a macrocyclic ligand, which allows the formation of a quadratic-antiprismatic coordination geometry with a relatively small degree of angle distortion.

The sandwich complex **2** displays alternatingly short [2.767(5), 2.716(7) Å] and long [3.328(9), 3.218(6) Å] Ag–S distances. Differences in the S–Ag–S angles for "short" and "long" bonds are, however, relatively small: *e.g.s.* S(1)–Ag(1)–S(3) 106.3(2), S(2)–Ag(1)–S(4) 108.8(2)°; S(1)–Ag(1)–S(1 a) 142.5(2), S(2)–Ag(1)–S(1 a) 144.6(2)°; S(2)–Ag(1)–S(2 a) 90.2(2), S(2)–Ag(1)–S(3 a) 90.7(2)°. Whereas the As atoms in the crown-shaped cycloarsathiane ring are close to being coplanar (± 0.043 Å), larger deviations of ± 0.132 Å from a best least-squares plane are necessary for the four sulphur atoms in order to accommodate the alternating short and long Ag–S bonds. This leads to significant changes in the bond and torsion angles displayed by the *K*^{4}*S, S′, S″, S‴* coordinated eight-membered ring in **2** in comparison to the free ligand. For instance, the S–As–S angles in **2** are on average [100.0(4)°] 3.2° narrower than those in **1** [average 103.2(6)°]. In contrast, coordination of Ag(I) leaves the As–S–As angles virtually unaffected with the average values being 97(1)° in **2** and 96.5(9) in **1**. A degree of alternation is observed for the ring torsion angles in the uncoordinated cyclotetramer, which lie in the absolute range 101.9–112.5° (Tab. V). Coordination of the silver (I) cation leads to a marked decrease in the torsion angles As(2)–S(2)–As(3)–S(3) and As(4)–S(4)–As(1)–S(1) from an average value of 106.5(3)° to 95(1)°. These changes for the more distantly coordinated sulphur atoms S(2) and S(4) are accompanied by a similar increase in the oppositely sited torsion angles As(1)–S(1)–As(2) and As(3)–S(3)–As(4)–S(4), which themselves involve the more closely coordinated atoms S(1) and S(3) as central atoms. These angles change from an average value of 107.7(1)° to 121(2)°. In contrast the remaining four torsion angles in the cycloarsathiane ring exhibit only minor alterations in the absolute angle range 0.3–2.2°.

Tab. V. Torsion angles (°) in **1–3**.

Compound	**1**	**2**	**3**
S(4)–As(1)–S(1)–As(2)	–111.1(1)	–112.7(3)	110.6(2)
As(1)–S(1)–As(2)–S(2)	107.7(1)	122.3(2)	–107.9(2)
S(1)–As(2)–S(2)–As(3)	–103.1(1)	–102.8(3)	105.0(2)
As(2)–S(2)–As(3)–S(3)	106.3(1)	94.2(3)	–107.0(2)
S(2)–As(3)–S(3)–As(4)	–112.5(1)	–113.7(3)	109.2(2)
As(3)–S(3)–As(4)–S(4)	107.8(1)	119.8(3)	–108.4(2)
S(3)–As(4)–S(4)–As(1)	–101.9(1)	– 99.7(2)	105.5(2)
As(4)–S(4)–As(1)–S(1)	106.6(1)	95.9(3)	–106.7(3)

It is interesting to compare the coordination geometry of the silver cations in **2** with that of an idealized quadratic antiprism. If one defines the

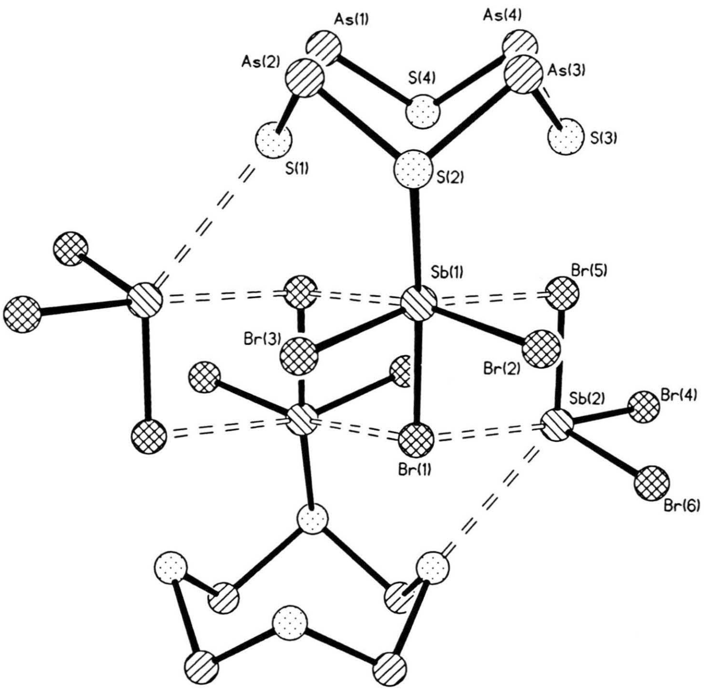

Fig. 4. Structure of $[cyclo\text{-}(C_2H_5AsS)_4]\cdot 2SbBr_3$ (**3**) with dashed bonds indicating weak Sb–Br and Sb–S interactions in the range 3.49–3.58 Å.

centres of the S_4 planes of the cycloarsathiane rings as respectively M and M′ then the observed torsion angles S–M–M′–S exhibit alternating average values of 41.6(5)° [*e.g.* S(2)–M–M′–S(2a)] and −48.4(4)° [*e.g.* S(2)–M–M′–S(3a)]. In comparison to the idealized S–M–M′–S torsion angle of 45° for a quadratic antiprism, the coordination polyhedron in **2** exhibits an 8% distortion towards a cube (Fig. 3). The degree of elongation may be gauged from the average value of the angle α = M–Ag–S. Despite the differing Ag–S distances, all four independent M–Ag–S angles in **2** lie in the range 52.7–56.0°, with an average value of 53.8(15)° relatively close to the characteristic value of 57° observed for transition metal complexes ML_8 [24]. A much greater degree of longitudinal distortion is observed in the cycloarsoxane complex $[Na\{cyclo\text{-}(C_2H_5AsO)_4\}_2]^+$, which exhibits an average α value of 47.2° [2].

Fig. 4 depicts the structure of $[cyclo\text{-}(C_2H_5AsS)_4]\cdot 2SbBr_3$ (**3**). Weak Sb–Br secondary bonds lead to the formation of a dimeric unit in the crystal lattice. S(2) of the cycloarsathiane ring adopts an axial position in the ψ-trigonal bipyramidal coordination sphere of Sb(1). A relatively weak secondary bond is indicated by the Sb–S distance of 3.099(5) Å, which may be compared to the range of values between 2.968(2) and 3.460(3) Å observed in the complexes $[9]aneS_3\cdot SbCl_3$ and $[18]aneS_6\cdot 2SbCl_3$ [6]. The antimony atoms in these complexes are each coordinated by three sulphur atoms from individual crown thiothers. This is also the case in $[9]aneS_3\cdot SbI_3$ [7], which exhibits a distorted octahedral geometry with narrow S–Sb–S chelating angles [74.0(1)–74.8(1)°] and relatively strong Sb–S bonds [2.840(2)–2.895(2) Å]. The adoption of a similar geometry in a hypothetical triethylcyclotriarsathiane complex $[cyclo\text{-}(C_2H_5AsS)_3]\cdot SbBr_3$ would presumably lead to unfavourably small S–Sb–S angles. The observation of only one further very weak Sb–S interaction [Sb(2)–S(a) 3.490(5) Å] in **3** is, however, somewhat surprising in view of the reported structures of $[9]aneS_3\cdot SbCl_3$ and $[9]aneS_3\cdot SbI_3$.

The present work indicates the potential of ethylcycloarsathiane $(C_2H_5AsS)_n$ as a multidentate macrocyclic ligand, which may be capable of stabilizing unusual coordination geometries as in the case of $[Ag\{cyclo\text{-}(C_2H_5AsS)_4\}_2]^+$ (**2**). As for the analogous cycloarsoxane $(C_2H_5AsO)_n$ a preference for the formation of cyclotetramer complexes is apparent. [3].

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