Self-Assembly of Copper(I) Halide Networks Containing Tetra- or Pentameric Ethylcycloarsoxane $(C_2H_5AsO)_n$ (n = 4, 5) as a Flexible Bridging Unit

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In complexes of ethylcycloarsoxane $(C_2H_5AsO)_n$, the oligomer size n is influenced by the coordinated metal atom. Cyclic tetramers are observed in the porous sheet structures of $^2_\infty[Cu_2Br_2\{cyclo\text{-}(C_2H_5AsO)_4\}_3]$ (**1**) and $^2_\infty[Cu_3I_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ (**2**), prepared by the reaction of the appropriate copper(I) halide with $(C_2H_5AsO)_n$ in acetonitrile. Both complexes contain $\mu\text{-}1\kappa As^1{:}2\kappa As^3$-coordinated $(C_2H_5AsO)_4$ ligands as molecular bridging units between individual copper(I) centres leading to large respectively 36- and 40-membered rings. An analogous bridging mode is found in the cyclic oligomers $[cyclo\text{-}\{ReBr(CO)_3\{\mu\text{-}[cyclo\text{-}(C_2H_5AsO)_4]\}\}_4]$ (**3**) formed by reacting $[ReBr(CO)_5]$ with $(C_2H_5AsO)_n$ in refluxing toluene. – In contrast both $[(NH_4)\{cyclo\text{-}(C_2H_5AsO)_5\}_2][Ag(SCN)]_2$ (**4**) and $^2_\infty[\{Cs[cyclo\text{-}(C_2H_5AsO)_5]_2\}Cu_2(\mu\text{-}I)I_2]$ (**5**) contain pentamers $(C_2H_5AsO)_5$, which coordinate the NH_4^+ and Cs^+ cations κ^5O in a pentagonal antiprismatic fashion. In **5**, prepared by self-assembly from CsI, CuI, and $(C_2H_5AsO)_n$ in acetonitrile, $[Cs[cyclo\text{-}(C_2H_5AsO)_5]_2]^+$ sandwich cations are linked through $\mu\text{-}1\kappa As^1{:}\text{-}2\kappa As^2$-coordinated $[Cu_2I_3]^-$ units into polymeric chains. This coordination pattern reflects the unique ring size adaptability of the ambidentate $(C_2H_5AsO)_n$ ligand.

^{1}H-NMR investigations have indicated that alkylcycloarsoxanes such as $(CH_3AsO)_n$ and $(C_2H_5AsO)_n$ are present in solution as a mixture of cyclic oligomers, of which cyclotrimers and cyclotetramers predominate[1,2]. However, our studies on the coordination properties of ethylcycloarsoxane have demonstrated that the dynamic reorganisation equilibria between these cyclic ionophores may be influenced by the addition of alkali metal cations[3]. For instance, the ring size in the sandwich complexes $[M\{cyclo\text{-}(C_2H_5AsO)_n\}_2]SCN$ (M = Na, n = 4; M = K, n = 5)[3] isolated from acetonitrile solution is clearly controlled by the radius of the central cation. A metal-mediated ring expansion from the predominant solution species has also been observed for complexes of the type $[\{M(CO)_3\}_2\{cyclo\text{-}(RAsO)_6\}]$ (M = Mo, R = CH_3[4], M = Cr, W, R = C_2H_5[2]), in which $M(CO)_3$ groups are coordinated facially by the upper and lower three arsenic atoms of a flattened As_6O_6 cuboctahedron.

In contrast, a size-directing influence of the metal atom is not apparent for complexes in which individual metal atoms are coordinated by only one of the arsenic atoms of a particular cycloarsoxane. For instance, the dinuclear complex $[\{Cp'Mn(CO)_2\}_2\{cyclo\text{-}(CH_3AsO)_4\}]$ (Cp' = $CH_3C_5H_4$) contains a bidentate cycloarsoxane $(CH_3AsO)_4$ with a bridging function[5]. This preferred solution ring size has also been found in the bi-, tri-, and tetradentate $(C_2H_5AsO)_4$ cyclotetramers of the polymeric copper(I) halides $^2_\infty[Cu_4Cl_4\{cyclo\text{-}(C_2H_5AsO)_4\}_3]$, $^2_\infty[Cu_3Br_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$, and $^2_\infty[Cu_6I_6\{cyclo\text{-}(C_2H_5AsO)_4\}_3]$ with respectively chain and layered structures[6]. The latter lamellar compounds demonstrate the potential of alkylcycloarsoxanes as multidentate organometallic building blocks for the construction of novel nanoporous solid-state structures.

These fndings prompted us to investigate the preparation of further polymeric ethylcycloarsoxane complexes with a reduced $M/(C_2H_5AsO)_n$ ratio, in the expectation that the increased presence of immobilised cyclic ionophores in a solid-state network could provide compounds with interesting ion-exchanging properties. We also provide further evidence for the size-directing influence of monovalent cations such as NH_4^+ and Cs^+ and have employed this principle in the self-assembly of a novel chain structure $^2_\infty[\{Cs[cyclo\text{-}(C_2H_5AsO)_5]_2\}Cu_2(\mu\text{-}I)I_2]$, in which the cyclopentamers exhibit a unique $\mu_3\text{-}1\kappa As^1{:}2\kappa As^2{:}3\kappa^5O$ coordination mode.

Results

$[Cu_3Br_4\{cyclo\text{-}(C_2H_5AsO_4)\}]^-$ units in the polymeric compound $^2_\infty[Cu_3Br_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ are linked through two bridging $1\kappa As^1{:}2\kappa As^3$-coordinated $(C_2H_5AsO)_4$ ligands and the shared edge of a four-membered Cu_2Br_2 ring into a layered structure[6]. Reduction of the $CuBr/(C_2H_5AsO)_n$ ratio of 1:3 (for n = 1) employed for this compound to 1:10 leads to the isolation of a novel ethylcycloarsoxane bridged polymeric copper(I) bromide $^2_\infty[Cu_2Br_2\{cyclo\text{]-}(C_2H_5AsO)_4\}_3]$ (**1**) with a tetrahedral metal coordination sphere as depicted in Figure 1. The copper atom Cu(1) adopts an axial siting relative to the As_4O_4 rings of the independent $(C_2H_5AsO)_4$ ligands, each of which exhibits a *twist-chair* conformation. These bridging ethylcycloarsoxane units connect individual copper(I) tetrahedra into a 6^3 net with large 36-membered potentially ionophoric

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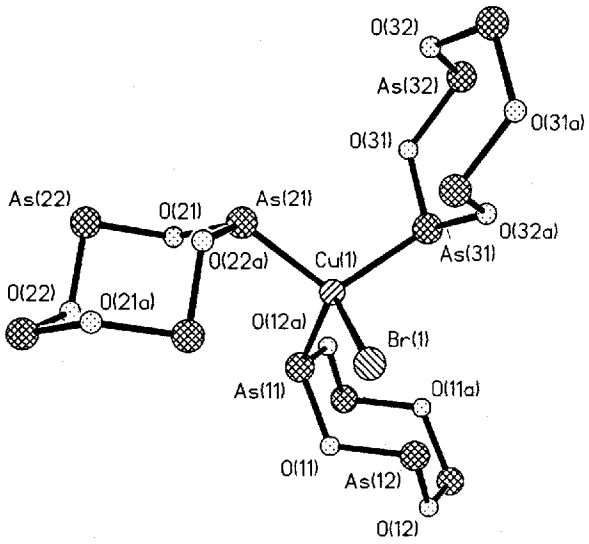
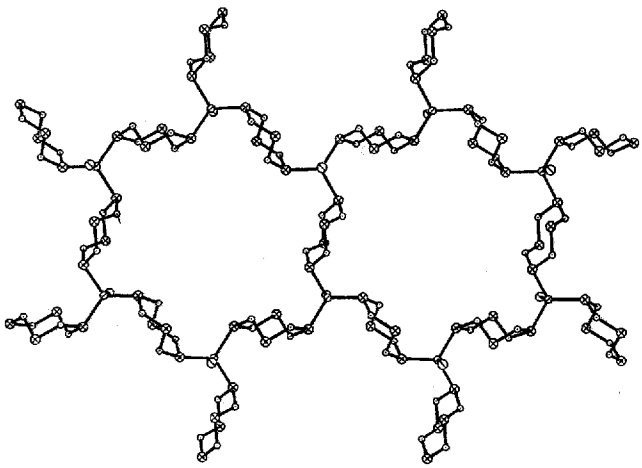
$Cu_6\{cyclo\text{-}(C_2H_5AsO_4)\}_6$ rings (Fig. 2). As observed for other metal complexes of alkylcycloarsoxanes, the As-O distances to the non-coordinated As atoms (range 1.819–1.835 Å) are significantly longer than those to the coordinated atoms As(11), As(21), and As(31) (range 1.746–1.790 Å). This difference is reflected in the O–As–O angles at the latter As atoms (range 101.5–103.7°), which are markedly wider than those of the noncoordinated atoms As(12), As(22), and As(32) (range 93.4–95.4°). In accordance with expectation, the terminal Cu(1)–Br(1) distance of 2.408(4) Å is much shorter than the distances to μ_2- and μ_3-bridging bromine atoms in $^2_\infty[Cu_3Br_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ of respectively 2.442(2)–2.455(2) and 2.524(2)–2.597(2) Å[6].

Figure 1. The copper(I) coordination sphere in $^2_\infty[Cu_2Br_2\{cyclo\text{-}(C_2H_5AsO)_4\}_3]$ **1** with ethyl groups omitted for clarity[a]



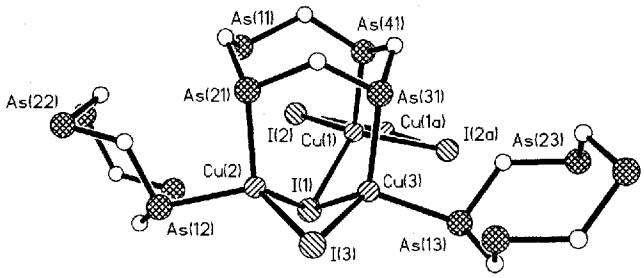
[a] Selected bond lengths and angles: Cu(1)–Br(1) 2.408(4), Cu(1)–As(11) 2.361(4), Cu(1)–As(21) 2.354(5), Cu(1)–As(31) 2.368(5) Å; Br–Cu(1)–As 103.0(2)–108.3(1), As–Cu(1)–As' 111.7(2)–115.8(2)°.

Figure 2. 6^3 net of the layered structure of **1** with ethyl groups omitted for clarity



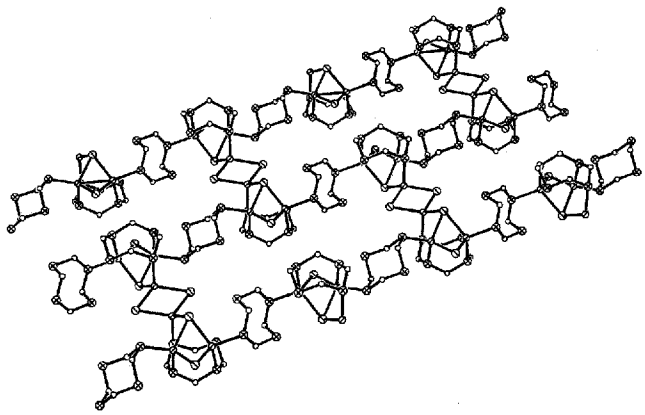
Attempts to prepare the analogous copper(I) iodide at a $CuI/(C_2H_5AsO)_4$ ratio of 1:10 afforded the compound $^2_\infty[Cu_3I_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ (**2**), the asymmetric unit of which is depicted in Figure 3. Although not strictly isostructural, both **2** and $^2_\infty[Cu_3Br_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ exhibit a similar triclinic sheet structure containing $1\kappa As^1{:}2\kappa As^3$- and $1\kappa As^1{:}2\kappa As^2{:}3\kappa As^3$-coordinated $(C_2H_5AsO)_4$ ligands (Fig. 4). Interestingly, the copper(I) bromide derivative is obtained at a much lower $CuBr/(C_2H_5AsO)_n$ ratio of 1:3 (for $n = 1$). A similar $CuI/(C_2H_5AsO)_n$ composition in the range 1:3–1:4.5 affords the copper(I) iodide-rich compound $^2_\infty[Cu_6I_6\{cyclo\text{-}(C_2H_5AsO)_4\}_3]$[6], a finding that is once again in accordance with the increased proclivity of copper(I) for the softer iodide anion in comparison to bromide.

Figure 3. The coordination spheres of the copper(I) atoms in $^2_\infty[Cu_3I_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ (**2**) with ethyl groups omitted for clarity[a]



[a] Selected bond lengths: Cu(1)–As(11) 2.413(3), Cu(1)–As(21) 2.373(3), Cu(2)–As(12) 2.400(3), Cu(2)–As(31) 2.364(3), Cu(3)–As(13) 2.370(3), Cu(1)–I(1) 2.693(3), Cu(1)–I(2) 2.639(2), Cu(2)–I(1) 2.648(2), Cu(2)–I(2) 2.642(3), Cu(3)–I(1) 2.677(3), Cu(3)–I(3) 2.660(3), Cu(3)–I(3a) 2.632(2) Å.

Figure 4. A layer $^2_\infty[Cu_3I_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ (**2**) with ethyl groups omitted for clarity



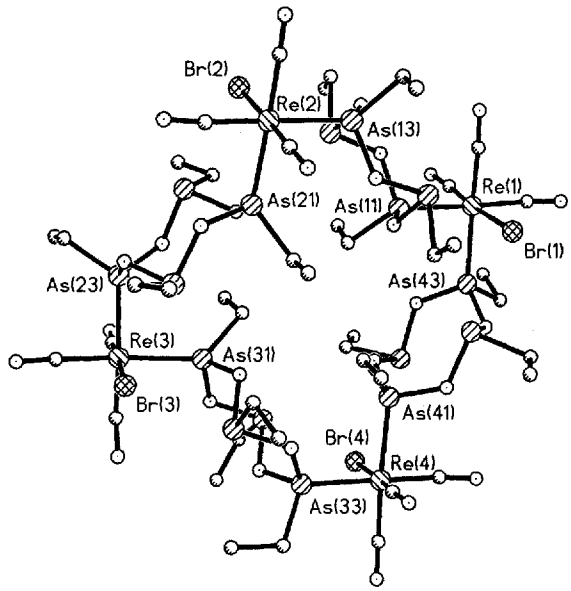
A crown-shaped As_4O_4 ring coordinated to three or four copper atoms is a familiar building block in the self-assembly of polymeric $(C_2H_5AsO)_4$ complexes of copper(I) halides, being observed in the chains of $^2_\infty[Cu_4Cl_4\{cyclo\text{-}(C_2H_5AsO)_4\}_3]$ and the sheets of $^2_\infty[Cu_3X_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$ (X = Br, I) and $^2_\infty[Cu_6I_6\{cyclo\text{-}(C_2H_5AsO)_4\}_3]$[6]. Such a crown is part of a $Cu_3I_2\{cyclo\text{-}(C_2H_5AsO)_4\}$ cage in **2**, that is connected through two centrosymmetric ethylcycloarsoxane ligands and a planar Cu_2I_2 unit into a layered structure with large 40-membered rings. Cu(1) and Cu(2) adopt axial positions relative to their respective As_4O_4 rings, both of which exhibit a *twist-chair*

conformation. Trends in the bond lengths and angles at the As atoms are similar to those in **1**, e.g. As–O distances to coordinated As atoms (range 1.775–1.815 Å) are on average shorter than those of the non-coordinated atoms As(11), As(22), and As(23) (range 1.794–1.837 Å). As for $^{2}_{\infty}[Cu_3Br_3\{cyclo\text{-}(C_2H_5AsO)_4\}_2]$, the copper–halogen bond lengths increase significantly on going from the μ_2-bridging atoms I(2) and I(3) (2.63–2.66 Å) to the μ_3-atom I(1) [2.693(2), 2.677(3) Å]. The Cu–I(1)–Cu′ angles vary in size from 61.7(1)° in the four-membered $(CuI)_2$ ring through 91.7(1)° for Cu(1)–I(1)–Cu(3) to 116.7(1)° for the copper atoms Cu(1) and Cu(2), that are coordinated by opposite arsenic atoms As(41) and As(21) of the crown-shaped $(C_2H_5AsO)_4$ ligand.

Both **1** and **2** and other analogous copper(I) halide complexes of ethylcycloarsoxane[6] contain exclusively μ-1κAs^1:2κAs^3-coordinated tetrameric $(C_2H_5AsO)_4$ ligands as molecular bridging units in their polymeric structures. The preferred employment of $(C_2H_5AsO)_4$ in the solid state could well be a result of the increased conformational flexibility of the cyclotetramer in comparison to the second major species in solutions of ethylcycloarsoxane, namely the cyclotrimer $(C_2H_5AsO)_3$. The preference for $(C_2H_5AsO)_4$ also leads to the formation of the cyclic oligomer $[cyclo\text{-}\{ReBr(CO)_3\{\mu\text{-}[cyclo\text{-}(C_2H_5AsO)_4]\}\}_4]$ (**3**) on reacting $[ReBr(CO)_5]$ with $(C_2H_5AsO)_n$ in refluxing toluene. As depicted in Figure 5 this cyclic tetramer exhibits a 20-membered ring in which $ReBr(CO)_3$ units are linked through μ-1κAs^1:2κAs^3-coordinated $(C_2H_5AsO)_4$ ligands in a twist-chair conformation. The asymmetric unit of **3** contains two independent cyclic tetramers, both of which display a similar structure with the Br atoms sited in alternating fashion above and below the best plane of the molecule. The relative shortening of the As–O bond lengths to coordinated As atoms is more pronounced than in **1** and **2**. Such distances exhibit an average value of 1.754(8) Å in **3** in comparison to 1.819(7) Å for non-coordinated As atoms. This change is accompanied by a concomitant widening of the average O–As–O angles from 95(1) to 103(1)°. In solution the presence of different conformers or possibly oligomers is indicated by the observation of more than the expected number of ^{1}H- and ^{13}C-NMR resonances for the ethyl groups of the coordinated and non-coordinated As atoms, e.g. 6 signals for the methyl C atoms. As a result of the increased degree of π-backbonding to the CO ligands in *trans* position to the coordinated ethylcycloarsoxane As atoms, the relevant carbonyl IR absorption bands are shifted to lower wavenumbers (2055, 1929 cm^{-1}) in **3** in comparison to $[ReBr(CO)_5]$[7] (2150, 2044 cm^{-1}). The position of the IR band for the carbonyl group in *trans* position to the bromide ligand remains effectively unchanged or going from $[ReBr(CO)_5]$ (1985 cm^{-1}) to **3** (1983 cm^{-1}).

Whereas samples of $(C_2H_5AsO)_4$ itself provide a wide uncontoured IR absorption band between 850 and 650 cm^{-1}, individual ν(As–O) and $\rho(CH_2)$ bands can be assigned in this range for complexes of the ligand[2,3]. As discussed previously, coordination of an As atom in $(C_2H_5AsO)_4$ leads to a marked shortening of the adjacent As–O bonds and

Figure 5. The cyclic tetramer of the first independent molecule of $[cyclo\text{-}\{ReBr(CO)_3\{\mu\text{-}[cyclo\text{-}(C_2H_5AsO)_4]\}\}]$ (**3**)[a]



[a] Selected bond lengths and angles: Re(1)–Br(1) 2.607(5), Re(1)–As(11) 2.518(4), Re(1)–As(43) 2.531(5) Å, As(11)–Re(1)–As(43) 93.7(1)°, O(11)–As(11)–O(14) 103(1), O(42)–As(43)–O(43) 101(1)°.

this state of affairs is reflected in a shift in the apposite ν(As–O) IR bands to higher wavenumber (**1** 781, **2** 775, **3** 786 cm^{-1}) in comparison to non-coordinated As atoms (**1** 747, **2** 756, **3** 757 cm^{-1}). The splitting of the ν(As–O) band is, therefore, characteristic for complexes containing cyclic tetramers $(C_2H_5AsO)_4$ with either 2 or 3 coordinated As atoms. In contrast the hexadentate cyclic hexamers of $[\{M(CO)_3\}_2\{cyclo\text{-}C_2H_5AsO)_6\}]$ (M = Cr, Mo, W)[2] exhibit only the ν(As–O) band for coordinated As atoms in the range 796–788 cm^{-1}. The $\rho(CH_2)$ vibrations absorb at respectively 708, 713 m, and 734 cm^{-1} in **1**–**3**.

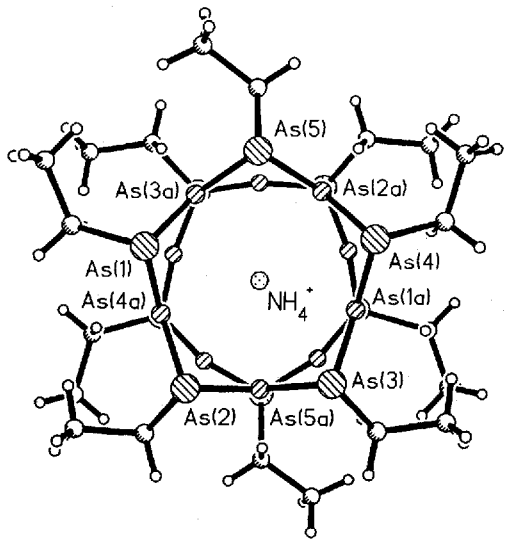
Alkali Metal Coordination

Complexes **1**–**3** contain eight-membered $(AsO)_4$ rings and should, therefore, be capable of coordinating *hard* cations. Although preliminary studies do, indeed, confirm the ability of the porous sheet structures of **1** and **2** to take up alkali metal halides from solution, we have not, as yet, been successful in obtaining defined compounds in this manner. However the alternative strategy of self-assembly does lead to the formation of the chain structure $^{2}_{\infty}[\{Cs[cyclo\text{-}C_2H_5AsO)_5]_2\}Cu_2(\mu\text{-}I)I_2]$ (**5**), in which Cs^+ cations are coordinated by the O atoms of two cyclic pentamers in a pentagonal antiprimatic fashion. A similar coordination mode is observed in $[K\{cyclo\text{-}(C_2H_5AsO)_5\}_2]SCN$[3] and $[(NH_4)\{cyclo\text{-}(C_2H_5AsO)_5\}_2][Ag(SCN)_2]$ (**4**) prepared in the course of this work. A size-directing influence of the alkali and ammonium cations is apparent in these three sandwich complexes.

Compound **4** was prepared by the reaction of NH_4SCN, AgSCN, and $(C_2H_5AsO)_n$ in acetonitrile. The ammonium cation is sited on a crystallographic inversion centre and

surrounded by ten O atoms at an average distance of 3.01(5) Å. Hydrogen atom positions could not be located in difference syntheses for this monocation. On ignoring the ethyl groups, the sandwich cation $[(NH_4)\{cyclo\text{-}(C_2H_5AsO)_5\}_2]^+$ displays D_{5d} symmetry with the cyclopentamer in a crown conformation (torsion angles ±111.6° to ±128.2°). The O atoms are approximately coplanar with deviations in the range 0.012–0.059 Å from the best least squares plane. It is instructive to compare the pentagonal antiprismatic geometry in **4** with that in the crown ether complexes $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2\ CH_3CN$ and $[(NH_4)(benzo\text{-}15\text{-crown-}5)_2]_2[UCl_6]\cdot 4\ CH_3CN$[8]. The reduced ring size of $(C_2H_5AsO)_5$ is reflected in the average O···O distance of 2.69 Å between adjacent O atoms in comparison to 2.84 and 2.78 Å in the above 15-crown-5 and benzo-15-crown-5 complexes. This leads to a longitudinal stretching of the pentagonal antiprism of **4**, which may be gauged from the distance of 1.96 Å of the ammonium N atom from the centre of the O_5 plane (Pl) of the cyclopentamer $(C_2H_5AsO)_5$. The analogous N···Pl distances in the crown ether complexes are respectively 1.83 and 1.81 Å. Associated with the increase in N···Pl in **4** is a concomitant narrowing of the O–N–O′ angles between adjacent O atoms to an average value of 53.1° as opposed to 56.5° and 56.0° in the crown ether complexes. The observed stretching of the pentagonal antiprism in **4** enables the retention of an average N–O distance of 3.01 Å similar to those of 3.00 and 2.96 Å in the 15-crown-5 and benzo-15-crown-5 sandwich complexes. An analogous lengthening of the coordination polyhedron was also observed for $[K\{cyclo\text{-}(C_2H_5AsO)_5\}_2]SCN$[3] in comparison to $[K(benzo\text{-}15\text{-crown-}5)_2]I$[9].

Figure 6. The $[(NH_4)\{cyclo\text{-}(C_2H_5AsO)_5\}_2]^+$ cation in **4**



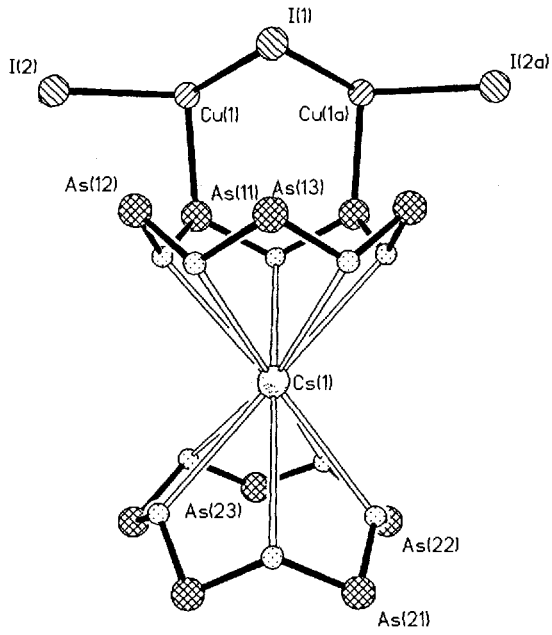
It is interesting to consider the possible patterns of N–H···O hydrogen bonding in **4**. In the cations $[(NH_4)(15\text{-crown-}5)_2]^+$ and $[(NH_4)(benzo\text{-}15\text{-crown-}5)_2]^+$, three of the five O atoms of the κ^5O ligands participate in such interactions. A similar disordered N–H···O interaction pattern involving one individual and one bifurcated hydrogen bond to the opposite two O atoms of the cyclic pentamer may be proposed for **4**.The $[Ag(SCN)_2]^-$ anions of this sandwich complex are involved in very weak secondary bonds to the cyclic pentamers $(C_2H_5AsO)_5$ as evidenced by the distances S(1)···As(5) 3.48, N(1)···As(3) 3.34, N(1)···As(4) 3.22, and Ag(1)···As(4) 3.39 Å.

The observation of a quadratic antiprism for $[Na\{cyclo\text{-}(C_2H_5AsO)_4\}_2]^+$ and pentagonal antiprisms for $[M\{cyclo\text{-}(C_2H_5AsO)_5\}_2]^+$ (M = K, NH_4) leads automatically to the question as to whether the analogous Cs sandwich cation will contain a cyclic pentamer or hexamer. Although we have been unable to isolate a complex of the type $[Cs\{cyclo\text{-}(C_2H_5AsO)_n\}_2]X$, this cationic unit is contained in $^2_\infty[\{Cs[cyclo\text{-}(C_2H_5AsO)_5]_2\}Cu_2(\mu\text{-}I)I_2]$ (**5**), the repeating unit of which is depicted in Figure 7. Despite its markedly larger cation radius, Cs^+ also exhibits a pentagonal antiprismatic geometry as found for the ethylcycloarsoxane complexes of K^+ and NH_4^+. The repeating unit of **5** displays a crystallographic mirror plane containing the atoms As(13), O(11), O(21), and I(1). In contrast to the first arsoxane ring [As(11)–As(13)], it was possible to resolve static disordering for the second cyclic pentamer [As(21)–As(23)]. The site of the third arsenic atom As(23) is displaced from the adjacent mirror plane giving rise to two possible positions for this atom and As(22), O(22), and O(23) in the unit cell. These atoms were assigned a site occupation factor of 0.5. As discussed for $[M\{cyclo\text{-}(C_2H_5AsO)_5\}]^+$ (M = K, NH_4), the pentagonal antiprismatic coordination sphere of the Cs^+ cation in **5** is once again markedly stretched in comparison to the analogous 15-crown-5 complexes $[Cs(15\text{-crown-}5)_2](WOF_5)$[11] and $[Cs(15\text{-crown-}5)_2]e^-$[12]. The degree of stretching may be gauged from the average distance of the central alkali metal cation to the centre of the O_5 plane (Pl) of the $(C_2H_5AsO)_5$ ligand. This parameter has a value of 2.33 Å in **5** as opposed to 2.05 Å in the 15-crown-5 complexes. The associated lengthening of the average Cs···O distance from respectively 3.14 and 3.15 Å in the crown ether sandwich complexes to 3.26 Å in **5** is similar to that observed for the analogous potassium coordination spheres (0.13 Å)[3].

$[Cs\{cyclo\text{-}(C_2H_5AsO)_5\}_2]^+$ pentagonal antiprisms are linked through bridging Cu_2I_3 units into the *zweier*[13] single chain depicted in Figure 8. Compound **5** provides the first example of an ambidentate alkylcycloarsoxane ligand coordinating through both the hard ring O atoms (κ^5O) and the softer As atoms ($\mu\text{-}1\kappa As^1\text{:}2\kappa As^2$). The tetrahedrally coordinated copper(I) atoms Cu(1) and Cu(2) bridge two cyclic pentamers $(C_2H_5AsO)_5$ to provide $[Cu_2I_3\{(C_2H_5AsO)_5\}_2]^-$ anions with Cu–As distances of 2.349(4) and 2.353(5) Å.

The formation of **5** from CsI, CuI, and $(C_2H_5AsO)_n$ provides confirmation for the postulated ionophoric nature of polymeric copper(I) halides containing alkylcycloarsoxane ligands as flexible bridging units. Our present work is now directed towards the preparation of similar compounds with covalent $(C_2H_5AsO)_n$-bridged copper(I) halide networks.

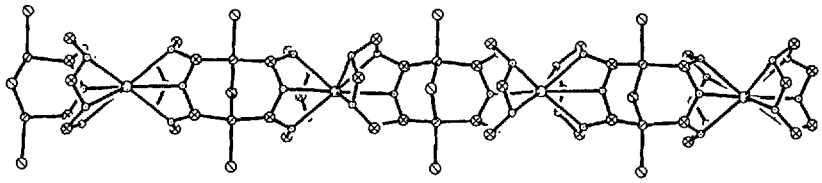
Figure 7. Repeating unit of the chain structure of $^{2}_{\infty}$[{Cs[*cyclo*-$(C_2H_5AsO)_5]_2$}$Cu_2(\mu$-I)I_2] (**5**)



[*cyclo*-{ReBr$(CO)_3${μ-[*cyclo*-$(C_2H_5AsO)_4$]}}$_4$] (**3**): $Re(CO)_5Br$ (0.293 g, 0.72 mmol) was added to a solution of *cyclo*-$(C_2H_5AsO)_n$ (0.289 g, 2.41 mmol for n = 1) in 10 ml of toluene which was refluxed for 10 min. After reduction in volume to 3 ml in vacuum the resulting solution was covered with hexane leading to formation of **3** as colourless crystalline precipitate over a period of 14 d. Yield 0.142 g (28%). – $C_{44}H_{80}As_{16}Br_4O_{28}Re_4 \cdot 0.5\ C_6H_5CH_3$ (3366.4): calcd. C 17.0, H 2.4; found C 16.8, H 2.7. – FAB-MS [*m/z* (%)]: 1309 (4) [ReBr$(CO)_3${$(C_2H_5$-$AsO)_4$}$_2$]$^+$; 1231 (5) [Re$(CO)_3${$(C_2H_5AsO)_4$}$_2$]$^+$, 830 (2) [ReBr$(CO)_3(C_2H_5AsO)_4$]$^+$ 751 (7) [Re$(CO)_3(C_2H_5AsO)_4$]$^+$. – ^{13}C NMR ($CDCl_3$): δ = 6.12, 6.18, 6.61, 6.84, 7.84, 7.91 (CH_2CH_3), 32.81, 33.64, 34.76, 37.87 (CH_2CH_3), 184.07, 184.63, 186.89 (*CO*). – IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} (m), 2933 (m), 2878 (m), 2055 (vs), 1983 (vs), 1929 (vs), 1495 (vw), 1456 (m), 1409 (m), 1382 (m), 1261 (vw), 1222 (w), 1084 (vw), 1030 (m), 987 (m), 973 (m), 786 (vs), 757 (vs), 734 (vs), 717 (vs), 614 (s), 598 (s), 580 (s), 537 (s), 524 (s), 494 (s), 482 (s), 457 (m), 438 (m), 356 (vw), 329 (w), 307 (m).

[(NH_4){*cyclo*-$(C_2H_5AsO)_5$}$_2$][$Ag(SCN)_2$] (**4**): AgSCN (0.100 g, 0.60 mmol) was added to a solution of *cyclo*-$(C_2H_5AsO)_n$ (0.723 g, 6.02 mmol for n = 1) and NH_4SCN (0.046 g, 0.60 mmol) in 25 ml of acetonitrile, which was subsequently stirred for 24 h. The resulting suspension, which still contained undissolved AgSCN was reduced to 15 ml in vacuum and left to stand at room temp. During a period of 14 d AgSCN slowly dissolved leading to formation of **4** as a white precipitate. A further crop of crystals of **4** was reaped by lowering the temperature to −20 °C. Yield 0.744 g (80%). – $C_{22}H_{54}AgAs_{10}N_3O_{10}S_2$ (1441.9): calcd. C 18.3, H 3.8, N 2.9; found 19.0, H 4.1, N 2.5. – ^{1}H NMR (CD_3CN): δ = 1.12 (t, 3H, $-CH_2CH_3$), 1.72 (q, 2H, $-CH_2CH_3$). – ^{13}C NMR (CD_3CN): δ = 6.03 (CH_2CH_3), 34.81 (CH_2CH_3). – IR (KBr): $\tilde{\nu}$ = 3220 cm^{-1} (m), 2967 (m), 2928 (m), 2871 (m), 2100 (s), 2053 (s), 1451 (s), 1413 (s), 1373 (s), 1221 (m), 1167 (w), 1029 (m), 970 (s), 742 (vs), 703 (vs), 586 (s), 553 (s), 459 (vw), 306 (m).

Figure 8. *Zweier* single chain of $^{2}_{\infty}$[{Cs[*cyclo*-$(C_2H_5AsO)_5]_2$}$Cu_2(\mu$-I)I_2] (**5**)



Experimental Section

All manipulation were performed in an Ar atmosphere in carefully dried solvents using standard Schlenk techniques. – FAB MS: Fison VG Autospec with 3-nitrobenzyl alkohol as matrix. – ^{1}H, ^{31}C NMR: Bruker AM 400. – FT-IR: Perkin-Elmer 1700 and 1760. – Elementary analyses: Carlo Erba 1106. – *cyclo*-$(C_2H_5AsO)_n$ was prepared by alkaline hydrolysis of $C_2H_5AsBr_2$ in benzene, followed by destillation, as described previously[1,14].

$^{2}_{\infty}$[Cu_2Br_2{*cyclo*-$(C_2H_5AsO)_4$}$_3$] (**1**): A solution of *cyclo*-$(C_2H_5AsO)_n$ (0.411 g, 3.42 mmol for n = 1) and CuBr (0.049 g, 0.34 mmol) in 10 ml of acetonitrile was stirred for 4 d and then cooled to −20 °C. After 2 d **1** could be isolated as a colourless crystalline precipitate. Yield 0.185 g (63%). – $C_{24}H_{60}As_{12}Cu_2Br_2O_{12}$ (1726.7): calcd. C 16.7, H 3.5; found C 16.6, H 3.6. – IR (KBr): $\tilde{\nu}$ = 2959 cm^{-1} (m), 2929 (m), 2872 (m), 1455 (m), 1405 (m), 1374 (m), 1280 (vw), 1219 (w), 1033 (m), 973 (m), 781 (vs, sh), 747 (vs), 708 (vs), 590 (s), 540 (s), 492 (s), 354 (vw), 302 (vw), 232 (vw).

$^{2}_{\infty}$[Cu_3I_3{*cyclo*-$(C_2H_5AsO)_4$}$_2$] (**2**): A solution of *cyclo*-$(C_2H_5AsO)_n$ (0.366 g, 3.05 mmol for n = 1) and CuI (0.058 g, 0.31 mmol) in 10 ml of acetonitrile was stirred for 4 d. Cooling to −20 °C afforded a colourless crystalline precipitate of **2**. Yield 0.062 g (39%). – $C_{16}H_{40}As_8Cu_3I_3O_8$ (1531.2): calcd. C 12.6, H 2.6; found C 12.5, H 2.7. – IR (KBr): $\tilde{\nu}$ = 2989 cm^{-1} (m), 2928 (m), 2871 (m), 1454 (m), 1404 (m), 1379 (m), 1221 (w), 1031 (m), 967 (m), 775 (vs, sh), 756 (vs), 713 (vs), 593 (s), 578 (s), 554 (s), 535 (s), 328 (vw), 303 (vw), 290 (w), 210 (vw).

$^{2}_{\infty}$[{Cs[*cyclo*-$(C_2H_5AsO)_5]_2$}$Cu_2(\mu$-I)I_2] (**5**): A solution of *cyclo*-$(C_2H_5AsO)_n$ (0.345 g, 2.90 mmol for n = 1), CsI (0.125 g, 0.50 mmol) and CuI (0.091 g, 0.50 mmol) in 20 ml of acetonitrile was stirred for 1 d at room temp. Slow evaporation of the resulting solution under argon afforded **5** as a colourless crystalline precipitate. Yield 0.443 g (82%). – $C_{20}H_{50}As_{10}CsCu_2I_3O_{10} \cdot 0.5\ CH_3CN$ (1861.0): calcd. C 13.6, H 2.8, N 0.4; found C 12.3, H 2.7, N 0.3. – IR (KBr): $\tilde{\nu}$ = 2961 cm^{-1} (m), 2927 (m), 2870 (m), 1451 (s), 1401 (m), 1376 (m), 1297 (w), 1221 (vw), 1029 (s), 969 (s), 746 (vs), 703 (vs), 585 (s), 544 (s), 307 (m).

X-Ray Structural Analyses: Siemens P4 diffractometer, graphite monochromator, Cu-K_α radiation (λ = 1.54184 Å) for **1**, Mo-K_α radiation (λ = 0.71073 Å) for **2**, **3**, and **4**, SHELXTL PLUS[15] programs for structure solution by direct methods and refinement by full-matrix least-squares. Absorption corrections were applied to the intensity data using DIFABS[16,17].

1: $C_{24}H_{60}As_{12}Cu_2Br_2O_{12}$, M = 1726.7, monoclinic space group $C2/c$ (No. 15), a = 25.077(5), b = 13.727(3), c = 18.396(4) Å, β = 114.51(3)°, 5762(2) Å^3, Z = 4, D_{calc} = 1.990 g · cm^{-3}, μ = 10.543 mm^{-1}. Crystal size 0.22 × 0.26 × 0.30 mm, t = 293 K, ω-scan: $2\Theta \leq 115.0°$ ($0 \leq h \leq 27$, $0 \leq k \leq 14$, $-20 \leq l \leq 18$), 4169 reflections collected, 3879 symmetry-independent reflections (R_{int} = 0.031), max./min. transmission: 0.063/0.042, 176 parameters refined, $w^{-1} = \sigma^2(F_o) + 0.0003\ F_o^2$, R = 0.069, Rw = 0.067 for 1706 reflections with $F > 4\sigma(F)$, largest difference peak: 0.97 eÅ^{-3}. Anisotropic temperature factors were introduced for the Br, As, Cu, and O atoms. Hydrogen atoms were not refined.

2: $C_{16}H_{40}As_8Cu_3I_3O_8$, M = 1531.2, triclinic space group $P\bar{1}$ (No. 2), a = 11.882(5), b = 13.838(4), c = 14.202(4) Å, α = 71.02(2), β = 73.33(3), γ = 69.93(3)°, 2057(1) Å^3, Z = 2, D_{calc} = 2.472 g · cm^{-3}, μ = 10.206 mm^{-1}. Crystal size 0.26 × 0.40 × 0.44 mm, T = 193 K, ω-scan: $2\Theta \leq 50.0°$ ($0 \leq h \leq 12$, $-15 \leq k \leq 16$, $-15 \leq l \leq 16$), 6806 reflections collected, 6801 symmetry-independent reflections, max./min. transmission: 0.058/0.014, 340 parameters refined, $w^{-1} = \sigma^2(F_o) + 0.0003\ F_o^2$, R = 0.060, Rw = 0.055 for 4256 reflections with $F > 3\sigma(F)$, largest difference peak: 1.51 eÅ^{-3}. Anisotropic temperature factors were introduced for all atoms except the carbon atoms of disordered ethyl groups. Hydrogen atoms were not refined.

3 · 0.5 $C_6H_5CH_3$: $C_{44}H_{80}As_{16}Br_4O_{28}Re_4$ · 0.5 $C_6H_5CH_3$, M = 3366.4, triclinic space group $P\bar{1}$ (No. 2), a = 11.730(3), b = 28.097(6), c = 28.700(7) Å, α = 93.7082), β = 92.74(2), γ = 95.52(2)°, V = 9382(4) Å^3, Z = 4, D_{calc} = 2.383 g · cm^{-3}, μ = 12.511 mm^{-1}. Crystal size 0.20 × 0.32 × 0.40 mm, T = 293 K, ω-scan: $2\Theta \leq 45.0°$ ($0 \leq h \leq 12$, $-30 \leq k \leq 30$, $-30 \leq l \leq 30$), 24045 symmetry-independent reflections, max./min. transmission: 0.045/0.021, 1044 parameters refined, $w^{-1} = \sigma^2(F_o) + 0.0004\ F_o^2$, R = 0.091, Rw = 0.070 for 10560 reflections with $F_o > 3\sigma(F_o)$, largest difference peak: 1.83 eÅ^{-3}. Anisotropic temperature factors were introduced for the Re, As, and Br atoms. The methyl group of the toluene molecule (site symmetry C_i) is disordered and was not included in the refinement. Hydrogen atoms were also not considered.

4: $C_{22}H_{54}AgAs_{10}N_3O_{10}S_2$, M = 1441.9, triclinic space group $P\bar{1}$ (No. 2), a = 10.667(3), b = 11.366(3), c = 11.918(4) Å, α = 113.28(2), β = 102.12(3), γ = 107.96(2)°, 1185(2) Å^3, Z = 1, D_{calc} = 2.021 g · cm^{-3}, μ = 7.487 mm^{-1}. Crystal size 0.22 × 0.32 × 0.34 mm, T = 213 K, ω-scan: $2\Theta \leq 55.0°$ ($-13 \leq h \leq 13$, $-14 \leq k \leq 13$, $0 \leq l \leq 15$), 5613 reflections collected, 5350 symmetry-independent reflections (R_{int} = 0.026), max./min. transmission: 0.134/0.082, extinction correction: χ = 0.00021(6), $F^* = F[1 + 0.002 \cdot \chi \cdot F^2/\sin(2\Theta)]^{-1/4}$, 239 parameters refined, $w^{-1} = \sigma^2(F_o) + 0.0001\ F_o^2$, R = 0.055, Rw = 0.053 for 4216 reflections with $F_o > 3\sigma(Fo)$, largest difference peak: 1.38 eÅ^{-3}. Anisotropic temperature factors were introduced for all atoms except hydrogen. These were included at calculated positions with group isotropic factors.

5: $C_{20}H_{50}As_{10}CsCu_2I_3O_{10}$ · 0.5 CH_3CN, M = 1861.0, orthorhombic space group $Pnma$ (No. 62), a = 23.219(7), b = 15.776(5), c = 13.770(6) Å, 5043(3) Å^3, Z = 4, D_{calc} = 2.450 g · cm^{-3}, μ = 9.914 mm^{-1}. Crystal size 0.34 × 0.40 × 0.44 mm, T = 193 K, ω-scan: $2\Theta \leq 48.0°$ ($0 \leq h \leq 26$, $0 \leq k \leq 18$, $0 \leq l \leq 15$), 4067 symmetry-independent reflections, max./min. transmission, 203 parameters refined, $w^{-1} = \sigma^2(F_o) + 0.0001\ F_o^2$, R = 0.089, R_w = 0.075 for 2084 reflections with $F_o > 4\sigma(F_o)$, largest difference peak: 2.17 eÅ^{-3}. Anisotropic temperature factors were introduced for Cs, I, As, Cu, and non-disordered O atoms. Hydrogen atoms were not refined.

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