Porous copper(I) coordination polymers containing both the cyclic ion ligating agent methylcycloarsoxane $(MeAsO)_4$ and rigid aromatic heterocycles as spacers

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Porous lamellar networks with flexible $[Cu_xI_y\{cyclo\text{-}(MeAsO)_4\}]$ ribbons bridged by either π–π stacked terminal benzonitrile ligands ($x = y = 2$), rigid *p*-diaminobenzene spacers ($x = y = 2$) or ionic $[Cs\{cyclo\text{-}(MeAsO)_4\}_2]^+$ sandwiches ($x = 3$, $y = 4$) may be constructed by self-assembly from CuI and $(MeAsO)_n$ in the presence of the respective structure-directing agents.

The rational design of porous solid-state coordination networks with potential ion exchange or molecular sieving properties has aroused considerable current interest.[1] Although the majority of known examples involve Ag^I or Cu^I centres separated by rigid organic spacers (*e.g.* piperazine, pyrazine, 4,4′-bipyridine and 4,4′-biphenyldicarbonitrile), a few encouraging reports of the employment of more flexible connecting ligands such as methylene bridged dichalcogeno ethers,[2] thioether macrocycles[3] or alkylcycloarsoxanes $(RAsO)_n$ (R = Me, Et; n = 4, 5)[4] have recently appeared. In analogy both to zeolites[5] and porous group 14 or 15 chalcogenidometalates,[6] such layers or frameworks might be expected to be capable of undergoing elastic deformations in response to different structure-directing agents or imbibed molecular guests. Our current extension of this line of coordination polymer design to networks containing both ion ligating alkylcycloarsoxanes and aromatic heterocycles has been motivated by the desire to construct multifunctional materials. To our knowledge, only one previous report of the self-assembly of an extended solid-state structure with both flexible and rigid spacers has appeared, namely that of ${}^{2}_{\infty}[\{Cu_2(C_3H_2O_4)_2(4,4'\text{-bipy})(H_2O)_2\}\cdot H_2O]$, in which small cyclic $[Cu(C_3H_2O_4)]_4$ tetramers ($C_3H_2O_4{}^{2-}$ = malonate) are linked through 4,4′-bpy ligands into a 4^4 net.[7]

We have recently demonstrated that ribbons of the type ${}^{1}_{\infty}[Cu_2X_2\{cyclo\text{-}(MeAsO)_4\}]$ (X = Cl, Br, I) can be joined into comparable square networks by employment of additional bridging $(MeAsO)_4$ ligands.[4c] When the self-assembly reaction‡ between CuI and $(MeAsO)_n$ is performed in PhCN instead of MeCN, the connectivity role of these linking cyclic tetramers is taken over by terminally coordinated solvent molecules, whose aromatic π-systems stack to generate the large channels depicted in Fig. 1.§ The pore size increases significantly from 0.41 × 0.72 nm (shortest transannular H···H contacts) in ${}^{2}_{\infty}[Cu_2I_2\{cyclo\text{-}(MeAsO)_4\}_2]^{4c}$ to 0.82 × 0.82 nm in ${}^{1}_{\infty}[\{Cu_2I_2(PhCN)_2[cyclo\text{-}(MeAsO)_4]\}\cdot PhCN]$ **1**, with the result that relatively large guest PhCN molecules can now be accommodated in the extended structure. In a second 4^4 net shown in Fig. 2, this design principle has been extended to bridging 1,4-diaminobenzene spacers. Deep-red crystals of the layered structure ${}^{2}_{\infty}[Cu_2I_2(p\text{-}H_2NC_6H_4NH_2)\{cyclo\text{-}(MeAsO)_4\}]$ **2** may be grown by carefully underlayering a $p\text{-}H_2NC_6H_4NH_2$–$(MeAsO)_n$ solution in MeCN with a CuI solution in the same solvent at 0 °C. Optical properties of zeolites with analogous imbibed parallel chromophore molecules such as *p*-nitroaniline are of considerable current interest.[8] The identical building principles of the triclinic lattices of **1** and **2** suggest that the construction of larger pores should be possible by employing longer rigid bidentate aromatic spacer molecules.

Alkylcycloarsoxanes $(RAsO)_n$ coordinate alkali metal ions M in sandwich complexes of the type $[M\{cyclo\text{-}(RAsO)_n\}_2]$, that are reminiscent of those formed by macrocyclic polyethers. The ring size of the crown-shaped $(RAsO)_n$ ligands is controlled by the volume of the central cation (M = Na, n = 4; M = NH_4, K, Cs, n = 5).[4b,9] Attachment of crown polyethers to solid supports such as silica gel has successfully been employed in commer-

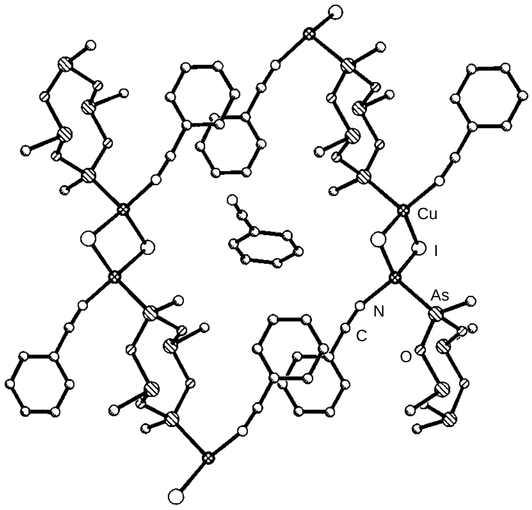

Fig. 1 Packing diagram for the π–π stacked ${}^{1}_{\infty}[Cu_2I_2(PhCN)_2\{cyclo\text{-}(MeAsO)_4\}]$ chains of **1**. Methyl groups have been omitted for clarity.

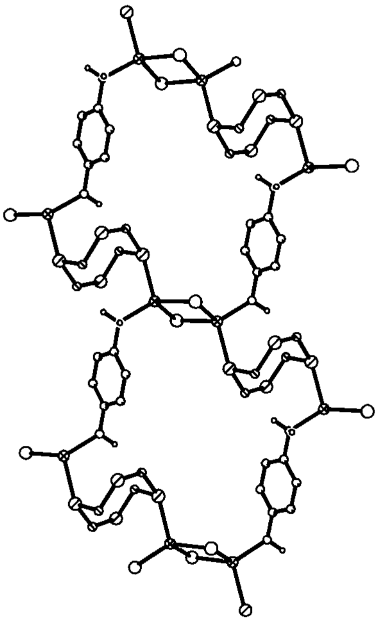

Fig. 2 Packing diagram for the lamellar ${}^{2}_{\infty}[Cu_2I_2(p\text{-}H_2NC_6H_4NH_2)\{cyclo\text{-}(MeAsO)_4\}]$ 4^4 net of **2**. Methyl groups have been omitted for clarity.

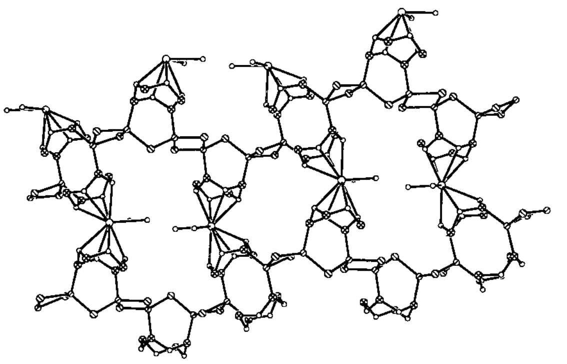

Fig. 3 Packing diagram for anionic ${}^{1}_{\infty}[Cu_3I_4\{cyclo\text{-}(MeAsO)_4\}_2]$ chains that are linked together through $[Cs\{cyclo\text{-}(MeAsO)_4\}_2]^+$ sandwiches into the porous sheet of **3**. Methyl groups have been omitted for clarity.

cially available solid-phase extraction systems (SPE).[10] Designed incorporation of such ion ligating agents into ordered solid-state networks offers, therefore, an attractive assignment for crystal engineering, that has been realized in the anionic ${}^{1}_{\infty}[Cu_3I_4\{cyclo\text{-}(MeAsO)_4\}_2]$ chains depicted in Fig. 3. Two water ligands were found to be necessary to complete the tenfold $\kappa^{10}O$ coordination spheres of the Cs^+ cations, which were used to direct the self-assembly of this structure, $[Cs(H_2O)_2][Cu_3I_4\{cyclo\text{-}(MeAsO)_4\}_2]$ **3**, from CuI and $(MeAsO)_n$ in MeCN–MeOH–H_2O. The presence of these H_2O molecules lends the larger cavities a degree of polar character and these contain disordered methanol molecules.

A DTA trace for **3** reveals initial endothermic loss of methanol and water (35–120 °C) followed by exothermic collapse of the solid-state network in the temperature range 122–149 °C. This indicates that the flexible sheet structure of **3**, whose individual $(MeAsO)_4$ and $[Cu_6I_8]^{2-}$ building blocks are illustrated in a schematic manner in Fig. 4, could be capable of imbibing a range of small polar molecules whilst retaining its integrity. We are currently studying whether this and similar anionic networks could be suitable for selective cation exchange.

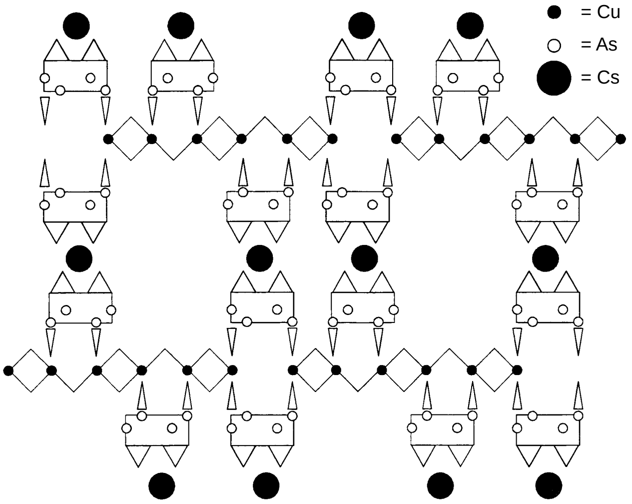

Fig. 4 A schematic diagram of the building principle of **3**, showing the μ-1 $\kappa As^1:2\kappa As^2$ and μ-$1\kappa As^1:2\kappa As^3$ bridging of $[Cu_6I_8]^{2-}$ units by different crown-shaped $(MeAsO)_4$ ligands which also simultaneously coordinate Cs^+ cations in a κ^4O fashion. Two water ligands complete the tenfold coordination sphere to the Cs^+ cations in the actual structure (Fig. 3).

Notes and References

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‡ ${}^{1}_{\infty}[\{Cu_2I_2(PhCN)_2[cyclo\text{-}(MeAsO)_4]\}\cdot PhCN]$ **1**: CuI (285.2 mg, 1.50 mmol) and $(MeAsO)_n$ (53.5 mg, 0.51 mmol for $n = 1$) were heated in 1.5 ml PhCN for 16 h in a sealed glass tube at 100 °C. The resulting yellow solution was left to stand at 4 °C to afford colourless crystals (81.2 mg, 64.3% yield).

${}^{2}_{\infty}[Cu_2I_2(p\text{-}H_2NC_6H_4NH_2)\{cyclo\text{-}(MeAsO)_4\}]$ **2**: 1,4-diaminobenzene (21.6 mg, 0.2 mmol) and $(MeAsO)_n$ (84.7 mg, 0.8 mmol for $n = 1$) were dissolved in 10 ml MeCN and the solution cooled to 0 °C. An acetonitrile solution (5 ml) of CuI (38.1 mg, 0.2 mmol) was layered under this solution leading to the formation of deep-red crystals (39.8 mg, 43% yield).

$[Cs(H_2O)_2][Cu_3I_4\{cyclo\text{-}(MeAsO)_4\}_2]\cdot 0.5MeOH$ **3**. A solution of CsI (95.2 mg, 0.5 mmol) in 1 ml H_2O–MeOH (1 : 4) was unified with 5 ml of an acetonitrile solution of CuI (65.0 mg, 0.25 mmol) and $(MeAsO)_n$ (211.9 mg, 2.0 mmol for $n = 1$) and left to stand at 20 °C to afford colourless crystals (130.0 mg, 46.5% yield). Satisfactory elemental analyses (C, H, As) were obtained for all compounds.

§ Siemens P4 diffractometer, graphite-monochromated Mo-Kα radiation, ω scans. The structures were solved using direct methods[11] and refined against F_o^2 by full-matrix least squares.[12] Hydrogen atoms were placed at calculated positions and allowed to ride on their parent atoms.

Crystal data: **1**: $C_{25}H_{27}As_4Cu_2I_2N_3O_4$, $M = 1114.06$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.740(2)$, $b = 9.254(2)$, $c = 11.732(2)$ Å, $\alpha = 101.84(3)$, $\beta = 101.24(3)$, $\gamma = 105.54(3)°$, $U = 862.8(3)$ Å^3, $Z = 1$, $F(000) = 526$, $D_c = 2.145$ g cm^{-1}, μ(Mo-Kα) = 6.86 mm^{-1}. Colourless tablet (0.37 × 0.39 × 0.54 mm), ψ-scan absorption corrections ($T_{min} = 0.30$, $T_{max} = 0.49$), 4603 unique reflectiions ($2\theta_{max} = 60°$) of which 3442 had $I \geqslant 2\sigma(I)$. Terminal reliability indices were $R_1 = 0.061$ [$I \geqslant 2\sigma(I)$], $wR_2 = 0.202$ for 207 refined parameters, $S = 1.12$, $\Delta\rho_{max} = 2.65$ e Å^{-3}, $\Delta\rho_{min} = -1.89$ e Å^{-3}.

2: $C_{10}H_{20}As_4Cu_2I_2N_2O_4$, $M = 912.84$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.861(2)$, $b = 9.021(2)$, $c = 9.199(2)$ Å, $\alpha = 63.19(3)$, $\beta = 84.64(3)$, $\gamma = 69.99(3)°$, $U = 545.7(2)$ Å^3, $Z = 1$, $F(000) = 422$, $D_c = 2.778$ g cm^{-1}, μ(Mo-Kα) = 10.81 mm^{-1}. Deep-red plate (0.12 × 0.17 × 0.32 mm), ψ-scan absorption corrections ($T_{min} = 0.27$, $T_{max} = 0.67$), 1840 unique reflections ($2\theta_{max} = 50°$) of which 1362 had $I \geqslant 2\sigma(I)$. Terminal reliability indices were $R_1 = 0.048$ [$I \geqslant 2\sigma(I)$], $wR_2 = 0.114$ for 111 refined parameters, $S = 1.02$, $\Delta\rho_{max} = 3.11$ e Å^{-3}, $\Delta\rho_{min} = -1.30$ e Å^{-3}.

3: $C_{8.5}H_{30}As_8CsCu_3I_4O_{10.5}$, $M = 1730.31$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.992(2)$, $b = 13.685(3)$, $c = 17.129(3)$ Å, $\alpha = 104.48(3)$, $\beta = 91.43(3)$, $\gamma = 107.21(3)°$, $U = 1938.3(7)$ Å^3, $Z = 2$, $F(000) = 1565$, $D_c = 2.965$ g cm^{-1}, μ(Mo-Kα) = 12.55 mm^{-1}. Colourless prism (0.39 × 0.49 × 0.60 mm), ψ-scan absorption corrections ($T_{min} = 0.080$, $T_{max} = 0.160$), 8768 unique reflections ($2\theta_{max} = 55°$) of which 5341 had $I \geqslant 2\sigma(I)$. Terminal reliability indices were $R_1 = 0.069$ [$I \geqslant 2\sigma(I)$], $wR_2 = 0.203$ for 302 refined parameters, $S = 1.03$, $\Delta\rho_{max} = 1.95$ e Å^{-3}, $\Delta\rho_{min} = -2.05$ e Å^{-3}. CCDC 182/793.

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