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# The structural definition of some novel adducts of stoichiometry CuX:dpex:MeCN $(2:1:1)_{(n)}$ , X = (pseudo-) halogen, dppx = Ph<sub>2</sub>E(CH<sub>2</sub>)<sub>x</sub>EPh<sub>2</sub>, E = P, As, Sb

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#### Abstract

Single-crystal X-ray studies have defined the structures of a number of novel adducts of the form CuX:dpex (2:1), X = (pseudo)halide, dpex = bis(diphenylpnicogeno)alkane, Ph<sub>2</sub>E(CH<sub>2</sub>)<sub>x</sub>EPh<sub>2</sub>, E = P, As, of diverse types, solvated with acetonitrile. CuBr:dpem (2:1)<sub>2</sub>. 2MeCN (E = both P, As) are tetranuclear, derivative of the familiar 'step' structure, while CuCl:dpph (MeCN solvate) and CuBr:dppe (MeCN solvate) yield one-dimensional polymers (i.e., x = 1, 2, 6 for dppx, x = m, e, h), as also does CuSCN:dpam (MeCN solvate). In CuI:dpsm:MeCN (3:1:2) ('dpsm' = Ph<sub>2</sub>Sb(CH<sub>2</sub>)SbPh<sub>2</sub>), CuI:dpsm (2:1)<sub>2</sub> 'step' units are connected into an infinite 'stair' polymer by interspersed (MeCN)CuI linkers.

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Keywords: Copper; Bis(diphenylpnicogeno)alkanes; Solvate complexes; X-ray

## 1. Introduction

Previous contributions [1–6] in the present sequence have described the structural characterization of unsolvated (i.e., no coordinated solvent) adducts of stoichiometry MX:dpex (1:1) [1–5] or (2:3)<sub>n</sub> [6], M = univalent coinage metal (copper(I), silver(I)), X = simple anion, usually (pseudo-)halide, or, when possible, oxyanions ClO<sub>4</sub>, NO<sub>3</sub>, carboxylate (spanning a range of basicities), dpex = Ph<sub>2</sub>E(CH<sub>2</sub>)<sub>x</sub>EPh<sub>2</sub>, bis(diphenylpnicogeno)-alkane (or, on occasion, bis(diphenylphosphino)-ferrocene, 'dppf'). Adducts of these combinations with the stoichiometry 2:1 are rather rare in the literature, being manifested by binuclear [M( $\mu$ -X)<sub>2</sub>( $\mu$ -*E*dpex-*E*')<sub>2</sub>M'] (AgO<sub>2</sub>CPh:dppf) [7], and tetranuclear 'step' structures for dppm (x = 1) with CuCl [8,9], Br [10–12], I [10,11] and AgCl [13]; there are numerous less immediately relevant examples involving gold(I). Polymeric forms are also evident in the Cuac:dppe (4:2) [14], Agac:dppm [15] and AgNO<sub>3</sub>:dpae [16] adducts, all complexes involving bridging oxyanion units. Further examples for M = Ag have been added in a recent study [17].

In this present sequence of papers, we describe a number of solvated (i.e., with coordinated solvent) adducts we have encountered, of diminished MX:L stoichiometric ratio, normally 2:1, here with copper(I) salts, with diverse dpex ligands, solvated with acetonitrile, yielding a variety of diverse forms of considerable novelty; an MeCN adduct of CuI with dpsm (=Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>), which, although of CuI:dpsm:MeCN (3:1:1) stoichiometry, is of a derivative extended 'stair polymer' form, also based on 'kernels' of 2:1 stoichiometry.

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# 2. Experimental

## 2.1. Syntheses

All syntheses and handling were carried out under nitrogen under Schlenk conditions. 'dpsm' was prepared according to the literature [18,19]. All other chemicals were purchased from Aldrich and Lancaster and used without further purification. Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm<sup>-1</sup> with a Perkin–Elmer System 2000 FT-IR instrument. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Mercury Plus Varian 400 NMR spectrometer (400 MHz for <sup>1</sup>H and 162.1 MHz for <sup>31</sup>P). H chemical shifts are reported in ppm versus SiMe<sub>4</sub>, P chemical shifts in ppm versus H<sub>3</sub>PO<sub>4</sub> 85%.

## 2.1.1. $CuBr:dppm:MeCN(2:1:1)_2(1)$

dppm (0.576 g, 1.5 mmol) was added at room temperature to an acetonitrile solution (20 ml) of CuBr (0.572 g, 4.0 mmol). After the addition, the solution was stirred for 48 h and then filtered. The colorless micro-crystalline precipitate was washed with acetonitrile to give complex 1 in 43% yield; m.p. 300-308 °C; a few crystals suitable for the X-ray work were obtained from the mother liquor on prolonged standing. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  2.10 (s, 6H, CH<sub>3MeCN</sub>) 3.45 (s, 4H, PCH<sub>2</sub>P), 7.0t, 7.14m, 7.28m, 7.30m, 7.58br (40H,  $C_6H_5$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K):  $\delta - 13.8$  (s br). IR (nujol, cm<sup>-1</sup>): 3052w (CH<sub>arom</sub>), 2292w, 2263w (CN), 1583w, 1570w (C···C), 523m, 510m, 472m, 444w, 432w, 421w, 373w, 355w, 235w, 203w, 177w, 157w. ESI MS (+): 975 [20]  $[Cu_2Br(dppm)_2]^+$ ; 1117 [10] 1118 [15]  $[Cu_3Br_2(dppm)_2]^+$ ; 1263 [30]  $[Cu_4Br_3(dppm)_2]^+$ ; 1503 [100]  $[Cu_3Br_2(dppm)_3]^+$ . Anal. Calc. for  $C_{54}H_{50}Br_2$ -Cu<sub>4</sub>N<sub>2</sub>P<sub>4</sub>: C, 51.28; H, 3.98; N, 2.21. Found: C, 51.34; H, 4.05; N, 2.18%.

# 2.1.2. CuBr:dpam:MeCN (2:1:1)<sub>2</sub> (2)

dpam (0.472 g, 1.0 mmol) was added at room temperature to an acetonitrile solution (20 ml) of CuBr (0.572 g, 4.0 mmol). After the addition, the solution was stirred for 24 h and then filtered. The colorless micro-crystalline precipitate was washed with acetonitrile to give complex **2** in 63% yield; m.p. > 300 °C; again a few more substantial crystals were obtained from the mother liquor on standing. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  2.10 (s, 6H, CH<sub>3MeCN</sub>), 3.3br (s, 4H, AsCH<sub>2</sub>As), 6.9–7.6br (40H, C<sub>6</sub>H<sub>5</sub>). IR (nujol, cm<sup>-1</sup>): 3045w (CH<sub>arom</sub>), 2291w, 2262w (CN), 1580w, 1570w (C···C), 585m, 552m, 328m, 312m, 267w, 177s br, 159s br, 123m, 100w, 73w. Anal. Calc. for C<sub>54</sub>H<sub>50</sub>As<sub>4</sub>Br<sub>2</sub>-Cu<sub>4</sub>N<sub>2</sub>: C, 45.02; H, 3.50; N, 1.94. Found: C, 45.31; H, 3.65; N, 1.97%.

# 2.1.3. CuBr:dppe: MeCN $(2:1:2)_{(\infty|\infty)}$ (3)

dppe (0.400 g, 1.0 mmol) was added at room temperature to an acetonitrile solution (20 ml) of CuCl (0.429 g, 3.0 mmol). After the addition, the solution was stirred for 12 h and then filtered. The colorless micro-crystalline precipitate was washed with acetonitrile to give complex **3** in 50% yield; m.p. 215–220 °C. It is insoluble in most common organic solvents, a few substantial crystals being obtained from the mother liquor on standing. IR (nujol, cm<sup>-1</sup>): 3042w (CH<sub>arom</sub>), 2290w, 2263w (CN), 1586w, 1569w (C···C), 552w, 514w, 484w, 216w, 203w. *Anal.* Calc. for  $C_{30}H_{30}Br_2Cu_2N_2P_2$ : C, 46.95; H, 3.94; N, 3.65. Found: C, 47.03; H, 4.07; N, 3.53%.

# 2.1.4. CuCl:dpph:MeCN $(2:1:1)_{(\infty|\infty)}$ (4)

dpph (0.454 g, 1.0 mmol) was added at room temperature to an acetonitrile solution (20 ml) of CuCl (0.298 g, 3.0 mmol). After the addition, the solution was stirred for 6 h and then filtered. The colorless micro-crystalline precipitate was washed with acetonitrile to give complex **4** in 63% yield; m.p. 200 °C. It is insoluble in most common organic solvents, a few substantial crystals being obtained from the mother liquor on standing. IR (nujol, cm<sup>-1</sup>): 3042w (CH<sub>arom</sub>), 2294w, 2262w (CN), 1613w, 1583w, 1567w (C···C), 548br, 519s, 484m, 426w, 441w, 423w, 176w. *Anal.* Calc. for C<sub>54</sub>H<sub>50</sub>Br<sub>2</sub>Cu<sub>4</sub>N<sub>2</sub>P<sub>4</sub>: C, 55.41; H, 5.09; N, 2.02. Found: C, 55.34; H, 5.03; N, 2.19%.

# 2.1.5. CuSCN:dpam $(2:1)_{(\infty|\infty)}$ (5)

dpam (0.472 g, 1.0 mmol) was added at room temperature to an acetonitrile solution (20 ml) of CuSCN (0.482 g, 4.0 mmol). After the addition, the solution was stirred for 24 h and then filtered. The colorless micro-crystalline precipitate was washed with acetonitrile to give complex **4** in 85% yield; m.p. > 300 °C; a few crystals suitable for the X-ray work were obtained from the mother liquor on prolonged standing. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  3.3 (br, 2H, AsCH<sub>2</sub>As), 6.9–7.3br (20H, C<sub>6</sub>H<sub>5</sub>). IR (nujol, cm<sup>-1</sup>): 3045w (CH<sub>arom</sub>), 2290w, 2265w (CN), 2135m, 2084m (SCN) 1580w, 1570w (C···C), 585m, 552m, 328m, 312m, 267w, 177s br, 159s br, 123m, 100w, 73w. *Anal.* Calc. for C<sub>27</sub>H<sub>22</sub>As<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: C, 45.32; H, 3.10; N, 3.91; S, 8.96. Found: C, 45.53; H, 3.25; N, 3.97; S, 9.03%.

#### 2.1.6. CuI:dpsm:MeCN (3:1:2) (6)

A few crystals of the colorless complex 6 were obtained by slow evaporation of a solution of millimolar stoichiometries (1:1) of copper iodide and dpsm in acetonitrile.

#### 2.2. Structure determinations

For some of the earlier determinations, unique single counter diffractometer data sets were measured  $(2\theta/\theta \text{ scan} \text{mode}; T \text{ ca. } 295 \text{ K};$  monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.7107_3 \text{ Å}$ ), Gaussian absorption corrections being applied, the 'observed' criterion being  $I > 3\sigma(I)$ ; for others, full spheres of CCD area-detector diffractometer data (Bruker AXS instrument,  $\omega$ -scans; T ca. 153 or 300 K) yielded  $N_{t(\text{otal})}$  reflections, these merging to N unique ( $R_{\text{int}}$  cited) after 'empirical'/multiscan absorption correction (proprietary software),  $N_{0}$  with  $F > 4\sigma(F)$  considered 'observed'

Table 1		
Selected geometries, l	MX:dppm(:MeCN) (4:2(:2)) (following the nome	nclature of Ref

E/M/X/solvent (phase)															
Distances (Å)	а	b	с	d	е	f	g	h	i	j	k	l	т	п	0
P/Ag/Br <sup>a</sup>	2.764(2) 2.742(3)	2.721(2) 2.734(2)	2.747(4) 2.735(2)	2.771(2) 2.846(3)	2.554(2) 2.535(2)	2.396(3) 2.402(3)	2.383(3) 2.380(4)	3.650(1)	4.116(2)	3.348(2) 3.346(1)	4.042(2) 3.988(2)	4.232(3) 4.181(3)	3.154(1) 3.307(2)	4.019(2) 3.859(2)	
P/Cu/Cl/(CH <sub>2</sub> Cl <sub>2</sub> ; C2/c) <sup>b</sup>	2.312(7)	2.740(5)	2.324(7)	2.357(6)	2.272(5)	2.196(5)	2.194(5)	3.468(5)	3.699(8)	2.914(4)	3.610(7)	3.750(9)	2.905(4)	3.494(7)	
((CH <sub>3</sub> ) <sub>2</sub> CO; P1) <sup>c</sup>	2.368(3)	2.697(3)	2.358(3)	2.387(3)	2.252(2)	2.203(3)	2.185(3)	3.628(2)	3.548(2)	2.992(2)	3.580(2)	3.723(3)	2.958(2)	3.423(2)	
Br(Pbca) <sup>d</sup>	2.575(2)	2.579(2)	2.523(2)	2.552(2)	2.338(2)	2.214(4)	2.184(4)	3.449(2)	3.830(2)	2.944(2)	3.832(2)	4.022(2)	3.180(2)	3.695(2)	
I(Pbca) <sup>e</sup>	2.785	2.729	2.634	2.711	2.51 <sub>0</sub>	2.230	2.216	3.671	4.116	2.684	4.284	4.174	3.108	3.349	
P/Cu/Br/MeCN <sup>f</sup> (mol. 1) (mol. 2)	2.455(1) 2.4511(9)	2.761(1) 2.638(1)	2.454(1) 2.497(1)	2.527(1) 2.570(1)	2.450(1) 2.473(1)	2.205(2) 2.204(2)	2.216(2) 2.218(2)	3.257(1) 3.104(1)	4.0866(9) 4.0367(8)	3.074(1) 3.090(1)	4.019(1) 3.995(1)	3.814(1) 3.948(1)	3.451(1) 3.597(1)	4.245(1) 4.383(1)	2.167(6) 2.062(5)
As/Cu/Br/MeCN <sup>f</sup> (mol. 1) (mol. 2)	2.4561(9) 2.4634(8)	2.6872(9) 2.5619(9)	2.423(1) 2.4687(9)	2.5144(9) 2.5725(9)	2.4558(9) 2.4632(9)	2.3222(9) 2.3296(8)	2.3382(8) 2.3383(8)	3.137(1) 2.916(1)	4.0802(8) 4.0937(7)	2.930(1) 2.9833(9)	4.0824(9) 4.0814(8)	3.876(1) 4.0183(8)	3.662(1) 3.853(1)	4.368(1) 4.6105(8)	2.030(5) 2.010(4)
Sb/Cu/I/MeCN <sup>f,g</sup>	2.6515(6)	2.6830(6)	2.6369(6)	2.6933(6)	2.6402(6)	2.5311(5)	2.5442(6)	2.9800(8)	4.4247(5)	2.8890(7)	4.4731(5)	4.1568(7)	4.260(1)	4.876(1)	
Angles (°) P/Ag/Br <sup>a</sup>	α 97.27(5) 96.29(6)	$\beta$ 83.87(5) 82.28(5)	γ 93.69(5) 94.15(5)	δ 74.13(4) 73.84(5)	ε 116.44(8) 115.00(9)	ζ 114.17(8) 121.3(1)	η 69.46(5) 72.53(5)	θ 78.49(5) 78.46(6)	i 98.67(6) 95.49(6)	k 144.58(9) 150.6(1)	λ 115.05(9) 109.6(1)	μ 98.67(5) 101.20(6)	v 94.37(5) 97.98(5)	ξ 113.9(6) 113.9(6)	s 1
P/Cu/Cl/(CH <sub>2</sub> Cl <sub>2</sub> ; C2/c) <sup>b</sup>	93.7(2)	88.3(2)	90.6(2)	69.3(1)	129.6(2)	114.8(2)	77.0(2)	78.7(2)	102.5(2)	130.0(2)	127.5(2)	108.0(2)	80.67(8)	110.4(10)	ī
(Me <sub>2</sub> CO; P1) <sup>b,c</sup>	88.70(6)	91.30(6)	89.93(5)	71.83(5)	130.79(4)	118.11(6)	76.96(5)	80.90(6)	101.00(5)	136.45(4)	121.98(6)	103.94(6)	88.42(4)	113.44(5)	ī
Br(Pbca) <sup>d</sup>	95.98(6)	84.02(6)	97.36(6)	70.03(6)	113.2(1)	116.1(1)	76.68(6)	74.45(6)	103.13(7)	142.5(1)	112.7(1)	104.18(7)	89.20(5)	114.32(6)	ī
I(Pbca) <sup>e</sup>	96.5	83.5	106.0	59. <sub>0</sub>	112.6	115.9	68. <sub>8</sub>	62.9	110.1	130.8	109.0	100.7	80.0	113.9	ī
P/Cu/Br/MeCN <sup>f</sup> (mol. 1) (mol. 2)	102.98(4) 104.93(3)	77.02(8) 75.07(3)	100.66(3) 102.12(3)	70.91(3) 72.77(3)	126.62(6) 120.18(5)	120.62(6) 116.72(6)	87.66(3) 91.50(3)	77.62(4) 76.88(3)	107.69(4) 104.76(3)	119.93(5) 118.71(5)	115.56(6) 114.74(6)	107.69(4) 105.85(3)	82.98(4) 82.42(4)	114.2(3) 116.2(3)	$\overline{1}$ $\overline{1}$
As/Cu/Br/MeCN <sup>f</sup> (mol. 1) (mol. 2)	104.98(3) 109.09(3)	75.02(3) 70.91(2)	105.84(3) 111.69(3)	68.47(3) 71.05(2)	121.55(4) 111.69(3)	118.30(4) 111.97(4)	94.89(3) 99.82(3)	73.80(3) 74.44(3)	110.35(3) 105.85(3)	115.79(3) 117.55(3)	110.63(3) 108.60(3)	105.18(3) 106.01(3)	75.16(4) 68.42(4)	111.2(2) 113.6(2)	ī ī
Sb/Cu/I/MeCN <sup>f,g</sup>	112.09(8)	67.91(2)	114.45(2)	65.02(1)	107.59(2)	116.97(2)	105.69(2)	66.39(1)	113.99(2)	109.04(2)	98.61(2)	103.63(2)	60.15(4)	119.5(2)	ī
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						$\begin{bmatrix} g \\ g \end{bmatrix}$ (S)	- <b>A</b>								

[24])

<sup>a</sup> Ref. [13]; <sup>b</sup> Ref. [7]; <sup>c</sup> Ref. [8]; <sup>d</sup> Ref. [12]; note that Ref. [10,11] records a similar (unsolvated) earlier determination in space group  $P_{2_1/c}$ ; <sup>e</sup> Ref. [9] (no s.u.'s available); <sup>f</sup> this work (1). In the MeCN solvates, N–Cu(2)–Br(1',2), E are: 101.5(2), 96.7(2), 112.3(2) (mol. 1), 114.74(6), 118.71(5), 116.2(2) (mol. 2) (E = P); 105.8(2), 100.9(1), 112.6(1) (mol. 1), 101.0(2), 105.7(2), 116.4(1) (mol. 2) (E = As). <sup>g</sup> In the dpsm complex, Cu(3)–I(1,2), I(3) (1 - x, 1 - y,  $\bar{z}$ ), N(3) are 2.6748(6), 2.6218(6), 2.6521(6), 1.989(3) Å; N(3)–Cu(3)–I(2,3), I(3) (1 - x, 1 - y,  $\bar{z}$ ) are 106.3(1), 111.0(1), 106.5(1)°; I(2)–Cu(3)–I(3), I(3) (1 - x, 1 - y,  $\bar{z}$ ) are 113.28(2), 106.01(2); I(3)–Cu(3)–I(3) (1 - x, 1 - y,  $\bar{z}$ ) 113.25(2)°. Cu(3)···Cu(2), Cu(3) (1 - x, 1 - y,  $\bar{z}$ ) are 2.6968(8), 2.9011(7), I(3)···I(2,3) (1 - x, 1 - y,  $\bar{z}$ ), I(1) 4.2546(7), 4.4044(5), 4.1979(7) Å.

The dihedral angle between the Cu(1,2)I(1,2) plane and the Cu(2,3)I(2,3) plane is  $63.82(4)^\circ$ , while that between the latter and the Cu(3,3')I(3,3') plane is  $58.67(3)^\circ$ .

and used in the full-matrix least-squares refinement, refining anisotropic displacement parameter forms for the nonhydrogen atoms,  $(x,y,z,U_{iso})_{\rm H}$  being constrained at estimated values unless otherwise noted. Conventional residuals *R*,  $R_{\rm w}$  (weights:  $(\sigma^2(F) + 0.0004F^2)^{-1}$ ) are cited on |F|at convergence. Neutral atom complex scattering factors were employed within the XTAL 3.7 program system [20]. Pertinent results are presented in the tables and figures, the latter showing 20 (room-temperature) or 50% (153 K) probability amplitude displacement envelopes for the nonhydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Variations in procedure, difficulties, etc., are noted as 'variata'. Full .cif depositions (excluding structure factor amplitudes) have been deposited with the Cambridge Crystallographic Data Centre, CCDC 244596, 286765–286769.

CuBr:dpem:MeCN  $(2:1:1)_2 \equiv C_{58}H_{56}E_4Br_4Cu_4N_4$ , E = P, As (1, 2). Triclinic, space group  $P\overline{1}$  ( $C_i^1$ , No. 2), Z = 2 tetramers.

E = P, M = 1506.8. a = 21.846(3) Å, b = 12.085(2) Å, c = 11.943(2) Å,  $\alpha = 82.04(2)^{\circ}$ ,  $\beta = 80.19(1)^{\circ}$ ,  $\gamma = 84.20(1)^{\circ}$ , V = 3067 Å<sup>3</sup>.  $D_{calc}$  (Z = 4 tetramers) =  $1.63_1$  g cm<sup>-3</sup>.  $\mu_{Mo} = 41$  cm<sup>-1</sup>; specimen:  $0.7 \times 0.20 \times 0.14$  mm;  $T_{min,max} =$  0.43, 0.59.  $2\theta_{max} = 50^{\circ}$ ;  $N_t = 21584$ , N = 10795 ( $R_{int} =$  0.029),  $N_o = 7600$ ; R = 0.043,  $R_w = 0.050$ .  $|\Delta \rho_{max}| = 1.38(8)$ e Å<sup>-3</sup>. Single-counter instrument, T ca. 295 K.

E = As, M = 1682.6. a = 21.892(3) Å, b = 12.079(2) Å, c = 11.990(2) Å,  $\alpha = 81.961(2)^{\circ}$ ,  $\beta = 80.581(2)^{\circ}$ ,  $\gamma = 84.164(2)^{\circ}$ , V = 3091 Å<sup>3</sup>.  $D_{calc}$  (Z = 2 tetramers) =  $1.80_8$  g cm<sup>-3</sup>.  $\mu_{Mo} = 61$  cm<sup>-1</sup>; specimen:  $0.45 \times 0.40 \times 0.35$  mm; ' $T_{min/max} = 0.43$ .  $2\theta_{max} = 58^{\circ}$ ;  $N_t = 29505$ , N = 14461 ( $R_{int} = 0.051$ ),  $N_o = 11754$ ; R = 0.044,  $R_w = 0.054$ .  $|\Delta \rho_{max}| = 1.7(2)$  e Å<sup>-3</sup>. CCD instrument, T ca. 153 K.

CuBr:dppe:MeCN (2:1:2)<sub>( $\infty$ | $\infty$ )</sub>(3) = C<sub>30</sub>H<sub>30</sub>Br<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub>P<sub>2</sub>, M = 767.4. Monoclinic, space group C2/c ( $C_{2h}^{6}$ , No. 15), a = 14.303(3) Å, b = 11.268(2) Å, c = 20.260(4) Å,  $\beta = 103.37(3)^{\circ}$ , V = 3177 Å<sup>3</sup>.  $D_{calc}$  (Z = 4 f.u.) = 1.60<sub>5</sub> g cm<sup>-3</sup>.  $\mu_{Mo} = 40$  cm<sup>-1</sup>; specimen:  $0.22 \times 0.20 \times 0.11$  mm; ' $T_{min/max} = 0.72$ .  $2\theta_{max} = 58^{\circ}$ ;  $N_{t} = 18385$ , N = 4019( $R_{int} = 0.041$ ),  $N_{o} = 2918$ ; R = 0.035,  $R_{w} = 0.039$ .  $|\Delta \rho_{max}| = 1.1(1)$  e Å<sup>-3</sup>. CCD instrument, T ca. 300 K.

CuCl:dpph:MeCN (2:1:1)<sub>( $\infty$ | $\infty$ )</sub> (4) = C<sub>32</sub>H<sub>35</sub>Cl<sub>2</sub>Cu<sub>2</sub>NP<sub>2</sub>, M = 693.6. Monoclinic, space group  $P2_1/c$ , a =21.595(5) Å, b = 17.045(4) Å, c = 17.541(4) Å,  $\beta =$ 95.155(4)°, V = 6430 Å<sup>3</sup>.  $D_{calc}$  (Z = 8) = 1.43<sub>3</sub> g cm<sup>-3</sup>.  $\mu_{Mo} = 16.1$  cm<sup>-1</sup>; specimen: 0.20 × 0.13 × 0.10 mm; ' $T_{min/max} = 0.62$ .  $2\theta_{max} = 58^{\circ}$ ;  $N_t = 76153$ , N = 16537( $R_{int} = 0.12$ ),  $N_o = 9248$ ; R = 0.058,  $R_w = 0.063$ .  $|\Delta \rho_{max}| =$ 1.5(3) e Å<sup>-3</sup>. CCD instrument, T ca. 153 K.

*Variata.* The copper atoms were modelled as disordered over pairs of sites, seemingly concerted, occupancies refining to 0.928(2) and complement. Cu. Cu distances are 0.67(3), 0.74(3) (strand 1), 0.81(2), 0.87(2) Å (strand 2). Concomitant minor halide components were not resolved, nor any involving lighter atoms.

CuSCN:dpam:MeCN (2:1:1)<sub>( $\infty$ | $\infty$ )</sub> (5)  $\equiv$  C<sub>29</sub>H<sub>25</sub>N<sub>3</sub>As<sub>2</sub>-Cu<sub>2</sub>S<sub>2</sub>, M = 756.6. Monoclinic, space group  $P2_1/c$ , a = 16.842(1) Å, b = 9.5845(8) Å, c = 19.509(2) Å, 
$$\begin{split} \beta &= 107.435(2)^{\circ}, \quad V = 3005 \text{ Å}^3. \quad D_{\text{calc}} \quad (Z = 4 \quad \text{f.u.}) = \\ 1.67_2 \text{ g cm}^{-3}. \quad \mu_{\text{Mo}} = 38 \text{ cm}^{-1}; \quad \text{specimen:} \quad 0.20 \times 0.20 \times \\ 0.08 \text{ mm}; \quad T_{\text{min/max}} = 0.49. \quad 2\theta_{\text{max}} = 58^{\circ}; \quad N_t = 33362, \quad N = \\ 7634 \quad (R_{\text{int}} = 0.078), \quad N_o = 4338; \quad R = 0.045, \quad R_w = 0.045. \\ |\Delta \rho_{\text{max}}| = 1.6(3) \text{ e Å}^{-3}. \quad \text{CCD instrument}, \quad T \text{ ca. } 300 \text{ K}. \end{split}$$

CuI:dpsm:MeCN (3:1:2)<sub>(∞|∞)</sub> (6) =  $C_{29}H_{28}Cu_3I_3N_2Sb_2$ , M = 1219.4. Triclinic, space group  $P\bar{1}$ , a = 11.435(2) Å, b = 12.485(2) Å, c = 12.599(2) Å,  $\alpha = 75.900(2)^\circ$ ,  $\beta = 81.396(2)^\circ$ ,  $\gamma = 89.975(2)^\circ$ , V = 1724 Å<sup>3</sup>.  $D_{calc}$  (Z = 2f.u.) = 2.34<sub>9</sub> g cm<sup>-3</sup>.  $\mu_{Mo} = 60$  cm<sup>-1</sup>; specimen: 0.32 × 0.20 × 0.17 mm; ' $T_{min/max} = 0.70$ .  $2\theta_{max} = 58^\circ$ ;  $N_t = 16642$ , N = 8257 ( $R_{int} = 0.022$ ),  $N_o = 7284$ ; R = 0.026,  $R_w = 0.034$ .  $|\Delta \rho_{max}| = 1.3(1)$  e Å<sup>-3</sup>. (x,y,z,  $U_{iso}$ )<sub>H</sub> refined. CCD instrument, T ca. 153 K.

# 3. Results and discussion

#### 3.1. Syntheses

The reaction of two or more equivalents of CuBr with one equivalent of bis(diphenylphosphino)methane (dppm), bis(diphenylarsino)methane (dpam), or 1,2-bis(diphenylphosphino)ethane (dppe) at room temperature in acetonitrile gave rise to compounds CuBr:dppm:MeCN (2:1:1)<sub>2</sub> (1), CuBr:dpam:MeCN (2:1:1)<sub>2</sub> (2), and CuBr:dppe:MeCN (2:1:2)<sub>( $\infty \mid \infty$ </sub>) (3), respectively. CuCl:dpph:MeCN (2:1:1)<sub>( $\infty \mid \infty$ </sub>) (4) (dpph = 1,6-bis(diphenylphosphino)hexane) and CuSCN:dpam:MeCN (2:1:1)<sub>( $\infty \mid \infty$ </sub>) (5) were synthesized from the same solvent by using the same procedure. Small crystals of the complex CuI:dpsm:MeCN (3:1:2) (6) in low yields were obtained by slow evaporation of a solution of



Fig. 1. Projection of tetranuclear CuBr:dpam:MeCN (4:2:2) (2) ((centro-symmetric) tetramer 1; tetramer 2 is similar); the E = P counterpart (1) is isomorphous.

millimolar stoichiometries (1:1) of copper iodide and bis(diphenylstibino)methane (dpsm) in acetonitrile.

The choice of solvent and the ligand to metal ratio are both determinants in the formation of the compounds, which, despite their solvation, are generally rather insoluble; they may be representative of more extensive arrays which present usually as deposits and may be polymers or polymeric mixtures, even less susceptible of structural characterization than the present. Normally when both reactants were mixed and stirred in a 1:1 ligand to metal molar ratio the well-known 1:1 adducts are obtained. Compounds 1 and 2 are soluble in acetonitrile and DMSO, and insoluble in alcohols and diethyl ether; they are moderately soluble also in chlorinated solvents. Conductivity measurements, as expected, indicated that complexes 1 and 2 are non-electrolytes not only in MeCN but also in dichloromethane solution, the values of  $\Lambda_M$  for these compounds being 1.0 and  $2.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively. The other compounds were too insoluble to yield useful data.

## 3.2. Spectroscopy

The infrared spectra of 1-5 (see Section 2) are consistent with the formulations proposed, showing all of the bands required by the presence of the bis(diphenyl pnicogeno)alkane donors [21]. The bands due to the P/As/Sb ligands are only slightly shifted with respect to those of the free donors. In the far-IR spectra of derivatives 1-4we assigned, on the basis of a previous report on phosphino silver(I) derivatives [22], the broad absorptions near 500 cm<sup>-1</sup> and those at 450–400 cm<sup>-1</sup> to Whiffen's y and t vibrations, respectively. No bands assignable to terminal Cu–Cl and Cu–Br stretching vibrations have been found. On the other hand, two broad bands at ca. 160 and



Fig. 2. Projections of CuBr:dppe:MeCN (2:1:1) $_{(\infty|\infty)}$  (3): (a) the unit cell down *b*, showing the disposition of the polymer strands relative to associated inversion centres in space group C2/c; (b) a single strand of the polymer.

180 cm<sup>-1</sup> have been detected in the spectrum of **1**. Analogous bands have been previously assigned to v(Cu-Cl) in complexes containing a bridging halide group [28].

Solution studies, being unlikely to reflect in detail or more generally the complexed polymeric forms present in the solid, should be considered with that caveat in mind. In the <sup>1</sup>H NMR spectra of **1**, **2** in CD<sub>3</sub>CN (see Section 2), the signals due to the diphosphine exhibit a different pattern relative to those found for the free donors, confirming the occurrence at least of partial complexation in solution. The bridging methylene resonances in **1** and **2** appear as broad singlets or resolved multiplets between 1.00 and 2.50 ppm generally downfield shifted with respect to those found in the free donors. The <sup>1</sup>H NMR spectra in DMSO of the derivatives **3–5** exhibit the same chemical shift values found in the free donors, suggesting complete disruption of the polymeric form.

The <sup>31</sup>P NMR spectrum (CD<sub>3</sub>CN solution) of derivative 1 exhibits a broad signal at -13.8 ppm ascribed to unidentified fluxional processes. The absorption is downfield shifted with respect to the corresponding signal in the free ligand.

The positive electrospray mass spectra of complexes 1 and 2 (the most relevant data are reported in Section 2) indicate that these derivatives persist as tetranuclear species also in a solution. The isotopic distribution of these species is in accord with the calculated composition. However, the major peaks are those derived from a trinuclear species containing a 1:1 ligand to metal ratio, positively charged consequent upon loss of a bromide group; no adducts containing MeCN were detected when the spectra were measured in acetonitrile. No multiply charged species were observed. The negative electrospray spectra of 1 and 2 are dominated by the presence of peaks due to [CuBr<sub>2</sub>]<sup>-</sup>. We have also studied solutions containing the CuBr and dpem in different ligand to metal molar ratios. We have observed that peaks due to  $[Cu_4Br_3(dpem)_2]^+$  are present in solution only when a large excess of the copper bromide (4:1) salt was employed, whereas when a 1:1 ligand to metal molar ratio was employed  $[Cu_3Br_2(dpem)_3]^+$  is the predominant species.  $[Cu_2Br(dppm)_2]^+$  and  $[Cu_3Br_2(dppm)_2]^+$  were present when a 1:2 ligand to metal molar ratio was employed, but all



Fig. 3. The two strands of the CuCl:dpph:MeCN  $(2:1:1)_{(\infty|\infty)}$  polymer (4) projected normal to their polymer axes: (a) propagated by the *c*-glide, and (b) by inversion centres. (c) The disorder in the binuclear cores. (d) Unit cell contents, projected down *b*.

peaks, with the exception of that, were due to  $[Cu_3Br_2(dppm)_3]^+$  when an excess of dppm was employed.

# 3.3. Structural studies

The structures of the present acetonitrile solvated 2:1 adducts of copper(I) salts MX with various L = dpex ligands have been defined by single-crystal X-ray methods in a diversity of oligo- and polymeric forms. The oligomers are, in fact all tetramers, all more or less derivative of the familiar 'chair' or 'step' structure, and we discuss them first in order of increasing complexity.

Archetypical examples of the 'step' tetramer have been described for a considerable variety of M/X (X = Cl, Br, I) combinations with unidentate group 15 ligands; in this form central and peripheral pairs of M and X atoms may be defined. The central M and X atoms are normally regarded as three-coordinate, leaving the M atom with the potential to coordinate a fourth unidentate ligand, while the peripheral M and X are two-coordinate, leaving the M atom potentially capable of coordinating up to two further donors. This possibility may be fully realized in rare MX:L(unidentate) (4:6) adducts, e.g., CuI:2-methylpyridine, the pair of peripheral adducts occupying both 'axial' and 'equatorial' sites [23]; more usually such adducts are of 4:4 MX:L stoichiometry, in which case the peripheral substituent is normally 'axial', in contrast to the infinite polymeric 'stair' structure where all substituents are 'equatorial', the 'axial' sites being occupied by polymer-extending linkages. In the simple MX:unidentate L (4:4) examples of the chair [24], the peripheral metal atoms are normally three-coordinate, leaving a fourth potential coordination site more or less exposed and thus remaining in the course of crystallization with excess of coordinating ligand or solvent, presumably, in the common examples, because of the relative bulk of the extant substituent visà-vis any second ligand or coordinating solvent capable of coordinating further. With bidentate dpex, usually dppm, the ligand usually spans peripheral and central metal atoms, the archetypical forms being found in the CuX (X = Cl, Br, I):dppm (4:2) [7–12] and AgCl:dppm (4:2) [13] adducts; the ligands spanning and coordinating at central and peripheral sites, as with the unidentate 4:4 complexes, not necessarily pre-empting polymer formation, but nevertheless presumably hindering it, similarly; as in the present work, access may certainly be possible in some circumstances to additional strongly coordinating ligands of small steric profile, namely acetonitrile. Topologically, the 'step' structure may be regarded as a 'cube' structure, severed along the centre of one face and unfolded; perhaps unsurprisingly, with relatively minor perturbations in respect of any or all of M, X, L or, even, lattice forces, it appears readily susceptible of 'distortion' to other conformations. Thus, with the ligand dppNH =  $P_2PNHPPh_2$ , the 4:2 AgBr adduct takes a form  $[(\mu_2-Br)(\mu_3-Ag)_2(\mu_4 Br_{2}(\mu_{3}-Ag_{2}(\mu_{2}-Br))$  with an 'octahedral' core, the four equatorial silver atoms spanned pairwise to either side by the  $\mu_2$ -bromines, and on the other equatorial edges by the dppNH ligands [25], while at a more fundamental level, one phase of CuCl:dppm (4:2) has very long  $M \cdots X$  distances within the central  $M_2X_2$  rhomb [9] (see below).

'Unsolvated' MX:dpem (4:2) (X = Cl, Br, I) 'step' structures thus far are predominantly structurally described for M = Cu, there being only one example for M = Ag (Cl/ dppm), in contrast to the MX:PPh<sub>3</sub> (4:4) arrays which, although not numerous, are described for both M = Cu, Ag [24]. Interestingly, in these MX:PPh<sub>3</sub> adducts, the peripheral trigonal metal atom (M = Cu or Ag) has an essentially planar environment ( $\Sigma$ (angles) = 358.0-359.8° for the examples listed in Ref. [24]), a state of affairs carrying over less rigorously to the present: for the unsolvated examples of Table 1, the sums are  $351_4$  (P/Ag/Cl), >358.3 (P/Cu/Cl,Br), 349.9° (P/Cu/I), suggesting that perhaps for some of these arrays (those with the largest M or X?) steric effects due to incorporation of the E x2 into a chelate may introduce strain. The present work shows the possibility of solvating these arrays (and their unidentate

Table 2		
Selected geometries.	CuCl:dpph:MeCN	$(2:1:1)_{(\infty \infty)}$ (4)

Atoms	Parameter	Atoms	Parameter
Distances (Å)		Angles (°)	
Cu(1)–Cl(1)	2.392(2),	Cu(1)-Cl(1)-Cu(2)	71.95(5), 71.08(5)
	2.383(2)		
Cu(1)– $Cl(2)$	2.449(2),	Cu(1)- $Cl(2)$ - $Cu(2)$	71.47(5), 71.10(5)
	2.438(2)		
Cu(2)-Cl(1)	2.313(2),	Cl(1)-Cu(1)-P(1)	126.07(7), 126.10(7)
	2.332(2)		100 1(0) 100 0(0)
Cu(2)– $Cl(2)$	2.278(2),	CI(1)-Cu(1)-N	102.1(2), 100.8(2)
$C_{\rm res}(1) = C_{\rm res}(2)$	2.273(2)	$C_{1}(2)$ $C_{2}(1)$ $D(1)$	11((2)(7)) 11((7)(7))
$\operatorname{Cu}(1)$ ···Cu(2)	2.764(1), 2.742(1)	CI(2) = CU(1) = P(1)	110.03(7), 110.70(7)
$C_{1}(1)$ $C_{1}(2)$	2.742(1) 3.482(2)	$C_{1}(2) = C_{1}(1) = N$	100.4(2) 100.7(2)
CI(1) $CI(2)$	3.480(2)	$\operatorname{Cl}(2)$ $\operatorname{Cl}(1)$ $\operatorname{IV}$	100.4(2), 100.7(2)
Cu(1) - P(1)	2.201(2).	P(1)-Cu(1)-N	114.8(2), 115.3(2)
	2.207(2)		
Cu(1)–N	2.056(7),	Cl(1)-Cu(1)-Cl(2)	92.01(6), 92.42(6)
	2.085(7)		
Cu(2)–P(2)	2.171(2),	Cl(1)-Cu(2)-Cl(2)	98.66(6), 98.15(6)
	2.172(2)		
		Cl(1)-Cu(2)-P(2)	128.16(7), 126.94(6)
		Cl(2)-Cu(2)-P(2)	132.98(6), 134.86(6)
		$\Sigma Cu(2)$	359. <sub>8</sub> , 360. <sub>0</sub>
Torsion angles (	~°) <sup>a</sup>		
α	47.1(5),	α′	-53.2(5), 58.0(5)
	43.7(5)		
β	-178.5(4),	$\beta'$	-177.4(4), 177.4(4)
	-178.2(5)		
γ	177.9(5),	$\gamma'$	174.0(5), -177.1(5)
	-178.8(5)		
0	-178.1(5),		
	180(-)		

The two values in each entry are for the major components in polymer strands 1,2; atoms X(3,4) in the latter are read as X(1,2).

<sup>a</sup> Polymer strand 1 is generated by a *c*-glide; strand 2 is generated by inversion centres within the two independent ligands to either side of the  $Cu_2X_2$  core; thus, all ligands are (quasi-) centrosymmetric.

EPh<sub>3</sub> counterparts?) coordinatively, with acetonitrile in the case of the CuBr/dppm adduct, **1**; the dpam counterpart of the latter, **2**, has also been isolated, the first such step tetramer adduct for dpam (E = As). In both of these cases, the planar three-coordinate array about the peripheral metal atom is augmented by coordination by the acetonitrile, which, necessarily, occupies the 'axial' site. There are two independent tetramers in the lattice, both centrosymmetric, one half of each contributing to the asymmetric unit. Geometries of the tetramer cores are tabulated comparatively with those of their unsolvated congeners in Table 1. In a number of situations, independent equivalent components of the same structure are available, showing considerable scatter, presumably consequent on lattice forces.

Nevertheless, on passing from the unsolvated dppm/CuBr tetramer to the solvated version, the expected trends in changes in the geometry are found, distances about the peripheral metal atom generally increasing, while, after further substitution of dppm by dpam, a weaker donor, there is a general shortening of the other distances about the copper atom (see Fig. 1).

The remaining adducts of gross CuX:dpex (2:1) stoichiometry are a diverse array for both X and dpex various, the majority polymeric with (E-dpex-E')Cu motifs linked diversely by anionic motifs to make one- or two-dimensional polymers; the solvent plays a significant role by increasing metal atom coordination numbers to 'normal' (four-coordinate) maximum values.



Fig. 4. (a) The double-stranded polymer of CuSCN:dpam:MeCN (2:1:1) $_{2(\infty|\infty)}$  (5) projected normal to its propagation axis; (b) the fused bicyclic motif.

The adducts CuX:dppx  $(2:1)_{(\infty|\infty)}$ , (a) X = Br, x = e (3), (b) X = Cl, x = h (4) are similar, in that the Cu(*P*-dppx-*P'*)Cu units are linked by Cu( $\mu$ -X)<sub>2</sub>Cu rhombs, whence the stoichiometry; the coordination number of the metal in such a ···-dppx-(*P*)Cu( $\mu$ -X)<sub>2</sub>Cu(*P*-dppx···) array being three, and both adducts being crystallized from acetonitrile, it is unsurprising to find the coordination numbers of the copper atoms augmented by acetonitrile coordination. Interestingly, however, we find the extent to which this occurs to differ between the two compounds, all copper atoms accepting fourth/acetonitrile donors in the CuBr:dppe adduct, but only one of each pair in the dpph adduct, which, moreover, contains a pair of independent strands with different internal symmetries.

In CuBr:dppe:MeCN  $(2:1:1)_{(\infty|\infty)}$  (3), one half of that formula unit, i.e., CuBr:0.5 dppe, comprises the asymmetric unit of the structure, a crystallographic inversion centre lying at the centre of the dppe ligand, the torsion in the central bond being obligate  $180^{\circ}/anti$ , with further inversion centres at the centres of the Cu(µ-Br)<sub>2</sub>Cu rhombs, which are obligate planar (Fig. 2). Cu–Br, Br' are somewhat unsymmetrical (2.5890(6), 2.4774(7) Å), with Cu–Br–Cu' 73.94(2)°; Br–Cu–Br' 106.06(2)°. Cu–N,P are 2.038(4), 2.232(1) with N–Cu–P 113.9(1)°; N–Cu–Br, Br' are 101.83(9), 103.91(9) and P–Cu–Br, Br' 110.17(3)°, 119.25(3)°, and torsion Cu–P–C(1)–C(1') –47.7(3)°.

The single-stranded polymer form is also found in CuCl:dpph (2:1) as crystallized from acetonitrile as a monosolvate (4); two independent strands are found, both similar in aspect, the first propagated by the *c*-glide, the second by inversion centres. This structure is remarkable in a number of aspects. The form of the polymer is that of familiar  $M(\mu-X)_2M$  units linked this time by one, rather than two (as in Ref. [4]) dppx ligands, demanding, at least incipiently, three- rather than four-coordinate metal atoms; there are two independent pseudo-symmetrically related polymer strands. Within each of the independent Cu<sub>2</sub>Cl<sub>2</sub> cores, one of the copper atoms is indeed, three-coordinate; the coordination number of the other is increased to four by coordination of the acetonitrile solvent molecule. While  $M_2Cl_2$  ( $M_2X_2$ ) rhombs of the present type are known for a variety of forms: EM(µ-X)<sub>2</sub>ME, EM(µ-X)<sub>2</sub>ME<sub>2</sub>, E<sub>2</sub>M(µ-X)<sub>2</sub>ME<sub>2</sub>, EE'M( $\mu$ -X)<sub>2</sub>MEE', E = N, P,..., we are not aware of any hitherto defined of the form  $EM(\mu-X)_2MEE'$ . Disorder is noted in the copper atoms, consistent across all four, raising the query as to whether there may be a minor component of cocrystallized polymer devoid of MeCN or with different MeCN coordination (for example). We believe it may be understood rationally in terms of interchange between the possibilities of three- and fourcoordinate sites: the small component adjacent to the three-coordinate (planar environment) copper(I) atom lies out of that plane and towards the acetonitrile, so that  $Cu \cdots N$  3.102(6), 3.046(7) Å, become supplanted by  $Cu' \cdots N$  2.40(3), 2.21(2) Å in the disordered form, while the disordered components of the four-coordinate Cu retreat towards a planar  $PCl_2$  environment, with  $Cu' \cdots N$  lengthening to 2.72(3), 2.89(2) Å. These distances associated with the disordered components are inherently imprecise and moreover, may be presumed to be associated with some degree of repositioning or reorientation of the chlorine and acetonitrile moieties, the minor fragments of these being unresolved. Values and trends in bond lengths and angles for the two copper types are essentially as expected. A consequence of the different symmetry generators of the two strands is that in strand 1 the ligand string is ht ht ht with the acetonitrile/-coordinated copper consistently associated with coordination of the one phosphorus atom. while in strand 2, the sequence is hh h'h' hh h'h' so that the two phosphorus atoms of one ligand are associated with the same type of copper atom. Both Cu<sub>2</sub>Cl<sub>2</sub> arrays are markedly non-planar, the 'folds' at the Cl. Cl lines being 48.36(8)°, 49.45(8)°; the agency of the fold is obscure, perhaps a consequence of 'lattice forces', since the packing of the array in the cell is impressive (Fig. 3) – the possibility that it may originate in 'crevice' coordination of the acetonitrile between both copper atoms is considered and discarded, the other Cu. N distances being 3.102(6), 3.046(7) Å, with a closely planar copper environment, although there is a precedent with pyridine and [cy<sub>3</sub>PAgI<sub>2</sub>AgPcy<sub>3</sub>], associated with considerable folding of the AgI2Ag array [26] (see Table 2).

The CuSCN:dpam (2:1) adduct, also solvated by acetonitrile and also polymeric, CuSCN:dpam:MeCN (2:1:1)<sub>2( $\infty \mid \infty$ </sub>) (5) (Fig. 4 and Table 3) is more complex and interesting. The polymer is double-stranded, propagated up the centre of a  $P2_1/c$  unit cell, by inversion and

Table 3		
Selected geometries, CuSCN:dpam:MeCN (2:1:1)	$ (\infty \infty) $	5)

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Cu(1)-As(1)	2.364(1)	Cu(2)–As(2)	2.379(1)
Cu(1)-S(1)	2.401(2)	Cu(2)-S(2)	2.516(2)
Cu(1)-S(2)	2.423(1)	$Cu(2) - N(1^{i})$	1.966(5)
Cu(1)–N(01)	1.966(5)	$Cu(2)-N(2^{ii})$	1.978(6)
S(1) - C(1)	1.654(6)	S(2)–C(2)	1.649(7)
C(1) - N(1)	1.152(7)	C(2)–N(2)	1.173(9)
Angles (°)			
As(1)-Cu(1)-S(1)	107.40(6)	As(2)-Cu(2)-S(2)	101.17(5)
As(1)-Cu(1)-S(2)	102.13(5)	$As(2)-Cu(2)-N(1^{iii})$	113.0(2)
As(1)-Cu(1)-N(01)	126.1(2)	$As(2)-Cu(2)-N(2^{ii})$	112.3(2)
N(01)-Cu(1)-S(1)	105.5(2)	$S(2)-Cu(2)-N(1^{iii})$	115.4(2)
N(01)-Cu(1)-S(2)	104.2(2)	$S(2)-Cu(2)-N(2^{ii})$	99.6(2)
S(1)-Cu(1)-S(2)	111.00(7)	$N(1^{i})-Cu(2)-N(2^{iii})$	114.1(2)
Cu(1)-S(1)-C(1)	103.3(2)	Cu(2)-S(2)-C(2)	98.8(2)
S(1)-C(1)-N(1)	178.0(7)	S(2)-C(2)-N(2)	178.3(5)
$C(1)-N(1)-Cu(2^{i})$	170.9(5)	C(2)-N(2)-Cu(2 <sup>ii</sup> )	159.7(5)
Cu(1)–N(01)–C(01)	167.6(6)	Cu(1)-S(2)-C(2)	99.1(2)
As(1)-C(0)-As(2)	112.9(3)	Cu(1)-S(2)-Cu(2)	114.75(7)

Transformations of the asymmetric unit: (i) x, 1 + y, z; (ii) 1 - x, 1 - y, 1 - z; (iii) x, 1 - y, z.

In the ring Cu(1)As(1)C(0)As(2)Cu(2)S(2), torsions in the bonds successively are  $-53.3(2)^{\circ}$ ,  $5.1(4)^{\circ}$ ,  $59.4(3)^{\circ}$ ,  $-59.2(2)^{\circ}$ ,  $1.22(7)^{\circ}$ ,  $42.53(7)^{\circ}$ , i.e., a 'boat' with Cu(1), As(2) at the prows.



Fig. 5. Two views of the polymer of CuI:dpsm:MeCN (3:1:1) $(\infty \mid \infty)$  (6): (a) projected down  $b^*$  and (b) within the unit cell, projected down a.

*b* translation. About (1/2, y, 1/2), the two strands are linked by the familiar eight-membered ring motif  $Cu\begin{pmatrix} SCN \\ NCS \end{pmatrix}Cu$ , disposed about a crystallographic inversion centre and comprised of {Cu(2)SCN(2)}<sub>2</sub> with the two SCN rods obligate parallel. The other two coordination sites about Cu(2) are made up of As(2) of the dpam ligand and the nitrogen of thiocyanate 1; As(1) of the dpam ligand bonds to Cu(1), bridged to Cu(2) by the sulfur of thiocyanate 2, thus creating a novel fused system of eight- and six-membered rings. The coordination environment of Cu(1) is completed by (terminal) acetonitrile and the sulfur of (translation-related) thiocyanate 1, propagating the polymer along *b*. S(1) is coordinated to one copper atom only, S(2) bifurcating a pair, one of each type, all with similar C–S–Cu angles (Table 3).

Although not of 2:1 MX:dpex stoichiometry, nor of any of the above forms, it is appropriate to record here the only dpsm (= *Sb*-dpsm-*Sb'*) complex we have hitherto obtained, namely, CuI:dpsm:MeCN  $(3:1:1(+1))_{(\infty|\infty)}$  (6), a novel infinite polymer containing the infinite step or 'stair polymer' motif, well known for adducts of the coinage metal halides [27] and derivative of the above 'step' structure (Fig. 5 and Table 1); the precautionary form of the stoichiometry above arises from the fact that one mole per formula unit of acetonitrile is coordinated and one not. The (CuI)<sub>( $\infty$ )</sub> stair polymer is of the usual form, of which [(MeCN)CuI]<sub>( $\infty$ )</sub> [27] may be regarded as archetypical; the present array, in fact, may be viewed as segmented into alternating sequences of MX:dpsm (4:2) 'step' tetramers interspersed by [(MeCN)CuI]<sub>2</sub> spacers. Geometries of the 'step' unit are given in Table 1 (footnote). The 'bite' of the free dpsm ligand (Sb. Sb) is 3.691(1) [28].

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