Synthesis, crystal structures and dynamic NMR studies of novel trinuclear copper(I) halide complexes with 2,5-bis[(diphenylphosphino)-methyl]thiophene

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Novel trinuclear copper(I) halide complexes with 2,5-bis[(diphenylphosphino)methyl]thiophene (dpmt), $[Cu_3(\mu_3\text{-}X)(\mu\text{-}X)_2(\mu\text{-}dpmt)_2]$ (X = I **1**, Br **2** or Cl **3**), have been synthesized and structurally characterised. They have unusual three-runged ladder structures with one triple-bridging and two double-bridging halide atoms. Two of the Cu^I are tetrahedrally co-ordinated and one, in the middle of the structure unit, has trigonal co-ordination geometry. The trinuclear $Cu_3(\mu_3\text{-}X)(\mu\text{-}X)_2$ framework shows some changes with halide anion X due to the size effect and intramolecular non-bonding $Cu \cdots Cu$ and $X \cdots X$ interactions. The NMR studies showed that the trinuclear framework is retained in solution for **1** (X = I), is in equilibrium with $Cu_3(\mu\text{-}X)_3$ for **2** (X = Br) and changes to $Cu_3(\mu\text{-}Cl)_3$ for **3** (X = Cl), an effect attributable to the decrease of halide size from iodide to chloride. The frameworks in the solutions of **2** and **3** exhibit fluxional behaviour involving bromine and chlorine mobility respectively.

Copper(I)–phosphine complexes have attracted increasing attention over the past decade due to their structural,[1–12] photochemical[6,10,12,13] and antitumor properties.[14] These complexes are of diverse structural architecture which is mainly influenced by the preparation conditions, steric properties such as the chain length, spatial arrangements and bulkiness of phosphine ligands and the co-ordinating ability and properties of the counter-ions. Thus copper(I) complexes with monodentate phosphine ligands exist as mononuclear $[Cu(PPh_3)_4]ClO_4$[2] and $[Cu(PPh_3)_3Cl]$,[3] binuclear $[\{Cu[P(totp)_3](\mu\text{-}X)\}_2]$[4] (totp = tri-*o*-tolylphosphine, X = Br or Cl) and $[Cu_2(PPh_3)_3(\mu\text{-}X)_2]$[5] (X = I, Br or Cl) and tetranuclear $[\{Cu(PPh_3)X\}_4]$ with pseudo-'cubane'[6] (X = I, Br or Cl) and open 'step'[7] (X = I or Br) structures. The dppm [bis(diphenylphosphino)methane] ligand has been reported to support mono- and bi-capping triangular-Cu_3 frameworks which are further stabilised by anions in $[Cu_3(\mu_3\text{-}Cl)_2(dppm)_3]Cl$,[8a] $[Cu_3(\mu_3\text{-}I)_2(\mu\text{-}I)(dppm)_2]$,[8b] $[Cu_3(dppm)_3(\mu_3\text{-}OH)][BF_4]_2$,[8c] $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu\text{-}dppm)_3]X_2$[8d] (R = Ph, X = BF$_4$; R = Bu^t, X = PF$_6$), $[Cu_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CR)(\mu_3\text{-}Cl)(dppm)_3]$-$X$[8e] (R = Ph, X = BF$_4$; R = Bu^t, X = PF$_6$) and $[(dppm)_3Cu_3$-$(\mu_3\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}p\text{-}\mu_3)Cu_3(dppm)_3]$.[8h] It can also stabilise the open 'step' tetrameric $[\{(CuX)_2(dppm)\}_2]$[9] (X = I, Br or Cl) and planar $[Cu_4(dppm)_4(\mu_4\text{-}E)][BF_4]_2$[10] (E = C{\equiv}C, S or Se) complexes. As 1,2-bis(diphenylphosphino)ethane (dppe) can co-ordinate as a bidentate bridging and chelating ligand, binuclear complexes are common in its copper(I) complexes $[\{CuX\text{-}(dppe)\}_2(\mu\text{-}dppe)]$[11] (where X is a monoanionic ligand such as N_3, Cl, OPh, PhCO$_2$, *etc.*). Among the above diverse mono-, bi-, tri- and tetra-nuclear arrangements, trinuclear Cu_3 frameworks are comparatively few and found only in copper(I) complexes with dppm[8] and bis(diphenylphosphino)-alkyl-/-arylamine (PNP)[12] ligands with triangular Cu_3 frameworks which are further bridged and stabilised by anions.

Meanwhile, the co-ordination chemistry of thiophene derivatives has been less developed.[15,16] The thiophene sulfur shows weak co-ordination ability and thiophene rings usually act as spacing units in the co-ordination compounds of Schiff bases derived from thiophene-2-carbaldehyde or thiophene-2,5-dicarbaldehyde.[16] Mathieu *et al.*[17] examined the co-ordination properties of 2,5-bis[2-(diphenylphosphino)ethyl]thiophene

and 2,5-bis[3-(diphenylphosphino)propyl]thiophene. In 2,5-bis-[2-(diphenylphosphino)ethyl]thiophene complexes with Mo^0, Co^I and Rh^I, the thiophene is η^1 (S) co-ordinated, while in 2,5-bis[3-(diphenylphosphino)propyl]thiophene complexes with Rh^I the η^2, η^3 and η^7 co-ordination modes have been established. The different behaviour indicates that the chain length between the phosphorus atom and the thiophene ring in the above two ligands affects the co-ordination properties of thiophene sulfur. In an attempt to study the co-ordination properties of thiophene derivatives in more detail, we have synthesized another novel ligand, 2,5-bis[(diphenylphosphino)methyl]thiophene (dpmt). With suitable bridging length and spatial arrangement, its complexes with copper(I) halides displayed unusual trinuclear Cu_3 frameworks with a three-runged ladder structure. Here we report the synthesis of dpmt and its novel trinuclear copper(I) halide complexes $[Cu_3(\mu_3\text{-}X)(\mu\text{-}X)_2$-$(\mu\text{-}dpmt)_2]$ (X = I **1**, Br **2** or Cl **3**). Crystal structure and dynamic NMR studies show that there are no direct copper(I)–thiophene sulfur interactions in the solid as well as in solution in the trinuclear copper(I) halide complexes.

dpmt
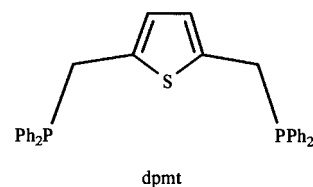
Results and Discussion

The ligand was synthesized by reaction of freshly distilled 2,5-bis(chloromethyl)thiophene with LiPPh$_2$ and characterised by MS, NMR and elemental analysis. It is stable in the solid state and unstable in CH$_2$Cl$_2$ and CHCl$_3$ solutions, being easily oxidised to form 2,5-bis(diphenylphosphorylmethyl)thiophene. Reaction of $[Cu(MeCN)_4]PF_6$ with dpmt in the molar ratio of 3:2 in acetonitrile, followed by additions of methanolic potassium halide or aqueous sodium chloride, gave the trinuclear complexes **1** (X = I), **2** (X = Br) and **3** (X = Cl) as colourless solids. These can also be synthesized by treating CuX with dpmt in dichloromethane followed by addition of methanol. Recrystallisation from dichloromethane–methanol gave single

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Table 1 Selected bond and contact distances (Å), angles (°) and some structural parameters for complexes for **1**–**3**

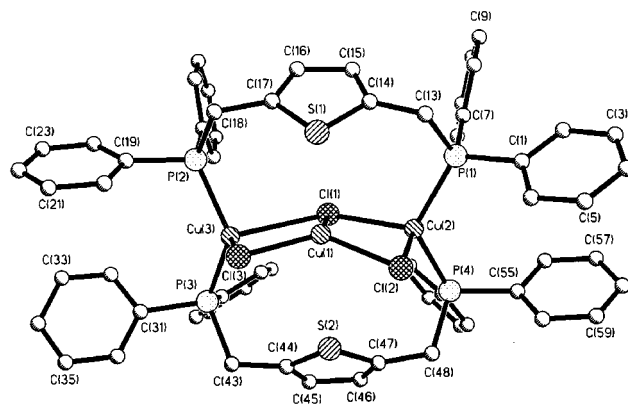|	**1** (X = I)	**2·2CH₂Cl₂** (X = Br)	**3·1.25CH₂Cl₂** (X = Cl)
Cu(1)–X(1)	2.542(2)	2.438(2)	2.377(2)
Cu(1)–X(2)	2.545(2)	2.419(2)	2.275(2)
Cu(1)–X(3)	2.577(2)	2.379(2)	2.237(2)
Cu(2)–X(1)	2.862(2)	2.563(1)	2.435(2)
Cu(2)–X(2)	2.678(2)	2.577(1)	2.456(2)
Cu(3)–X(1)	2.744(2)	2.791(1)	2.757(2)
Cu(3)–X(3)	2.724(2)	2.482(1)	2.340(2)
Cu(2)–P(1)	2.273(2)	2.254(2)	2.253(2)
Cu(2)–P(4)	2.273(2)	2.245(2)	2.242(2)
Cu(3)–P(2)	2.255(3)	2.250(2)	2.248(2)
Cu(3)–P(3)	2.264(3)	2.249(2)	2.241(2)
X(1)–Cu(1)–X(2)	120.02(6)	113.01(5)	107.87(7)
X(1)–Cu(1)–X(3)	120.65(6)	119.88(5)	116.61(8)
X(2)–Cu(1)–X(3)	119.17(6)	120.08(5)	127.40(8)
P(1)–Cu(2)–P(4)	131.33(9)	123.65(6)	122.20(7)
P(1)–Cu(2)–X(2)	104.99(6)	102.41(5)	102.53(7)
P(4)–Cu(2)–X(2)	102.17(6)	101.57(5)	101.86(7)
P(1)–Cu(2)–X(1)	105.35(7)	110.27(5)	112.19(6)
P(4)–Cu(2)–X(1)	105.32(7)	112.08(5)	113.58(6)
X(2)–Cu(2)–X(1)	105.33(4)	104.01(3)	100.51(6)
P(2)–Cu(3)–P(3)	124.30(10)	126.58(6)	126.30(7)
P(2)–Cu(3)–X(3)	103.09(8)	105.34(5)	105.57(7)
P(3)–Cu(3)–X(3)	103.69(8)	109.29(5)	111.91(7)
P(2)–Cu(3)–X(1)	106.78(8)	99.35(5)	100.56(6)
P(3)–Cu(3)–X(1)	109.21(8)	109.65(5)	108.60(6)
X(3)–Cu(3)–X(1)	108.86(4)	104.35(3)	100.45(6)
Cu(1)–X(1)–Cu(3)	65.32(4)	64.85(3)	66.47(5)
Cu(1)–X(1)–Cu(2)	65.84(4)	70.40(3)	73.84(5)
Cu(3)–X(1)–Cu(2)	131.15(4)	132.77(3)	137.94(7)
Cu(1)–X(2)–Cu(2)	68.70(4)	70.45(3)	75.24(6)
Cu(1)–X(3)–Cu(3)	65.16(4)	70.87(4)	76.41(7)
Cu(1)···Cu(2)	2.949(2)	2.885(2)	2.891(2)
Cu(1)···Cu(3)	2.857(2)	2.819(2)	2.832(2)
Cu(2)···Cu(3)	5.104(3)	4.907(3)	4.648(3)
X(1)···X(2)	4.406(2)	4.051(2)	3.761(3)
X(1)···X(3)	4.448(2)	4.189(2)	3.926(3)
Cu(1)···S(1)	2.971(2)	2.659(2)	2.645(2)
Cu(1)···S(2)	3.134(2)	3.339(2)	3.341(2)
S(1)···Cu(1)···S(2)	175.99(8)	172.26(5)	168.76(7)
Mean deviation of Cu₃X(1) plane/Å	0.008	0.164	0.146
Mean deviation of Cu(1)X₃ plane/Å	0.023	0.140	0.142
Mean deviation of Cu₃X₃ plane/Å	0.019	0.159	0.156
Deviation of Cu(1) from Cu₃X₃ plane/Å	0.046	0.349	0.341

Fig. 1 Perspective view of the structure of [Cu₃(μ₃-Cl)(μ-Cl)₂-(μ-dpmt)₂] **3** with atomic numbering scheme

framework constructed of one triple-bridging, atom X(1), two double-bridging X atoms X(2) and X(3), two tetrahedrally co-ordinated copper atoms Cu(2) and Cu(3) and one trigonally co-ordinated atom Cu(1), in the middle of the trinuclear structure unit. Atoms Cu(2) and Cu(3) are each co-ordinated to the phosphorus donor of two bridging dpmt molecules, one bridging halide and one μ₃-bridging halide. The two thiophene rings are *syn* sandwiching the Cu₃(μ₃-X)(μ-X)₂ plane. Structures involving a mixed copper(I) stereochemistry of tetrahedral and trigonal chromophores and both triple- and double-bridging X have been found in the tetranuclear open 'step' [{Cu(PPh₃)-X}₄][7] and [{(CuX)₂(dppm)}₂][9] (X = I, Br or Cl). The structures of complexes **1**–**3** have some similarities with these open 'step' molecules, but differ from them by the virtual planarity of the trinuclear Cu₃(μ₃-X)(μ-X)₂ frame. Obviously the dpmt ligands with a suitable bridging length and spatial arrangement play important roles in stabilising the planar trinuclear Cu₃(μ₃-X)-(μ-X)₂ framework. Such a 'three-runged ladder' structure is comparatively uncommon and has so far been found only in trinuclear rhodium(I) complexes [Rh₃(μ-dpmp)₂(CO)₃I₂]BPh₄[18a] and [Rh₃(μ-dpmp)₂(CO)I₄]BPh₄[18b] {dpmp = bis[(diphenylphosphino)methyl]phenylphosphine} in which the planar trinuclear Rh₃(μ₃-I)(μ-I)(μ-CO) or Rh₃(μ₃-I)(μ-I)₂ planes are bridged by two dpmp ligands.

As previously noted,[5,7,9] the Cu–X bond distances for tetrahedrally co-ordinated Cu(2) and Cu(3) are longer than those for trigonally co-ordinated Cu(1) and decrease with the halide anions from iodide to chloride. The longest Cu–X bond distance is 2.862(2) Å in **1**, 2.791(1) Å in **2** and 2.757(2) Å in **3**. Such long distances suggest that the above three bond interactions are comparatively weak. As the size of the bridging halogen atoms decreases along the sequence I > Br > Cl the X(2)–Cu(2)–X(1) and X(3)–Cu(3)–X(1) angles decrease and Cu(3)–X(1)–Cu(2), Cu(1)–X(2)–Cu(2) and Cu(1)–X(3)–Cu(3) angles increase. The X–Cu(1)–X angles are all within 1° of an ideal 120° for trigonal planar co-ordinated copper(I) in **1**, but deviate increasingly from the ideal value from **2** [X = Br, 113.01(5), 119.88(5), 120.08(5)°] to **3** [X = Cl, 107.87(7), 116.61(8), 127.40(8)°]. The mean deviation of Cu(1) from the corresponding Cu₃X₃ mean plane is 0.046 Å in **1**, 0.349 Å in **2** and 0.341 Å in **3**, all towards S(1), so that the Cu(1)···S(1) distance decreases with halide anions in the above three trinuclear complexes: 2.971(2) Å in **1**, 2.659(2) Å in **2** and 2.645(2) Å in **3**.

The stereochemical changes with the halide anions in the above three structures, to some extent, are due to the size effects of the different halide anions on the trinuclear Cu₃(μ₃-X)(μ-X)₂ frameworks and intramolecular non-bonding Cu···Cu and X···X interactions. Size effects of halide anions on structural changes have been found in trinuclear [Rh₃(μ-dpmp)₂(CO)₃X₂]-BPh₄[18a,c] (X = I, Br or Cl). In [Rh₃(μ-dpmp)₂(CO)₃I₂]BPh₄[18a,c]

crystals suitable for structure determinations. Complexes **1**–**3** were found stable in solution as well as in the solid state, but single crystals turned opaque on standing in air.

Structures of complexes 1–3

In order to investigate any systematic structural changes with the halide anions, complexes **1**–**3** were structurally characterised. They displayed a similar 'three-runged ladder' structure where the Cu₃(μ₃-X)(μ-X)₂ units were bridged by two dpmt ligands above and below the trinuclear plane. Fig. 1 shows a representative perspective drawing of complex **3**. Selected bond distances and angles are listed in Table 1. To the best of our knowledge, complexes **1**–**3** are the first examples of trinuclear copper(I) complexes with a 'three-runged ladder' structural

and [Rh$_3$(μ-dpmp)$_2$(CO)I$_4$]BPh$_4$,[18b] which have similar structural features to our reported complexes, only iodide anions can bridge the planar Rh$_3$(μ$_3$-I)(μ-I)(μ-CO) or Rh$_3$(μ$_3$-I)(μ-I)$_2$, while the bromide and chloride anions are not large enough to act as μ$_3$ planar ligands. Thus [Rh$_3$(μ-dpmp)$_2$(CO)$_3$X$_2$]BPh$_4$[18a,c] (X = Br or Cl) have slightly different structural features [the two tridentate bridging dpmp ligands determine the Rh$_3$(μ$_3$-I)(μ-I)-(μ-CO) or Rh$_3$(μ$_3$-I)(μ-I)$_2$ planes]. Teo and Calabrese[19] have systematically studied the structures of (R$_3$Y)$_4$M$_4$X$_4$-type complexes (R = Ph or Et; Y = P or As; M = Cu or Ag; X = Cl, Br or I) and made an unequivocal conclusion that their stereochemistries are to a significant extent dictated by intramolecular *non-bonded* van der Waals interactions which are a function of the size of the metal, the bridging X and the terminal ligands. In our three trinuclear [Cu$_3$(μ$_3$-X)(μ-X)$_2$-(μ-dpmt)$_2$] complexes the Cu(2)$\cdots$Cu(3) separation decreases with the halide anion from iodide [**1**, 5.104(3) Å] to bromide [**2**, 4.907(3) Å] and to chloride [**3**, 4.648(3) Å] due to the decreasing atom size. Distortion of the planar Cu$_3$(μ$_3$-X)(μ-X)$_2$ framework in **2** and **3**, to some extent, can minimise the repulsions between Cu$\cdots$Cu and X$\cdots$X as shown in the X$\cdots$X distances [Cl$\cdots$Cl 3.761(3) and 3.926(3); Br$\cdots$Br 4.051(2) and 4.189(2); I$\cdots$I 4.406(2) and 4.448(2) Å]. These distances are all greater than or close to normal van der Waals contacts (*viz.* Cl$\cdots$Cl 3.60; Br$\cdots$Br 3.90; I$\cdots$I 4.30 Å)[20] suggesting that these halogen–halogen interactions are strongly repulsive. The Cu$^I\cdots$S contact distances in the range 2.89–3.44 Å were found in other systems containing thiophene units[16] and were considered to be weak or non-bonding interactions. Copper(I)–sulfur bond distances are in the range 2.23–2.48 Å for co-ordinated sulfurs.[1] Co-ordination of thiophene sulfur has been established in [M(sttp)Cl][21] (M = Fe^{2+}, Ni^{2+} or Cu^{2+}, Hsttp = 5,10,15,20-tetraphenyl-21-thiaporphyrin) with M–S bond distances of 2.388 (M = Fe^{II}), 2.296(1) (M = Ni^{II}) and 2.335(2) Å (M = Cu^{II}), *fac*-[Mo(CO)$_3$L][17a] [Mo^0–S 2.569(1) Å] and [Rh(CO)L][ClO$_4$][17a] [Rh^I–S, 2.318(1) Å] {L = 2,5-bis-[2-(diphenylphosphino)ethyl]thiophene}. The fact that the Cu(1)$\cdots$S(1) distances in the range 2.645(2)–2.971(2) Å are longer than the sum of the covalent radii (2.21 Å),[22] whilst the S(1)–C(14), S(1)–C(17), S(2)–C(44) and S(2)–C(47) bond distances are comparable with 1.714(2) Å in free thiophene,[23] together with corroborating solution NMR studies, suggest that there are no direct bonded interactions between Cu^I and thiophene sulfur in our complexes. The copper–copper distances are in the range 2.819(2)–2.949(2) Å in **1**–**3**, shorter than those found in 'cubane' [Cu$_4$X$_4$(PPh$_3$)$_4$][6] (X = I, Br or Cl) [2.874(5)–3.164(4) Å] and 'step' [Cu$_4$X$_4$(PPh$_3$)$_4$][7] (X = I or Br) [2.835(3)–3.448(3) Å], and comparable with those found in 'step' [{(CuX)$_2$(dppm)}$_2$][9] (X = I, Br or Cl) [2.682(7)–3.180(2) Å], indicating that there are no direct Cu$\cdots$Cu interactions.

Trinuclear copper(I) complexes though comparatively rare can be found in some reduced forms of ascorbate oxidase.[24] Some spatial Cu$_3$ arrangements together with the tricopper(I) site of ascorbate oxidase are shown in Fig. 2. The ligand dppm is the appropriate supporter in Cu$_3$ framework (i)[8] which are further mono- or bi-capped by acetylide, alkynyl, halide, isocyanide and WS$_4$ anions. In Cu$_3$ framework (ii)[25] S-donor edge-bridging ligands such as ethane-1,2-dithiolate, S$_4$, S$_6$, Me$_3$PS and (PhO)$_2$P(S)NC(S)NEt$_2$ are needed to stabilise the structure framework. N-Donor ligands have recently been developed to support the triangular Cu$_3$ framework (iv)[26] as models of the active site of ascorbate oxidase; as no co-ordinated anions are involved in bridging, Cu$\cdots$Cu distances in structure framework (iv) are comparatively long. In our reported Cu$_3$ framework (iii) the new ligand dpmt with suitable bridging length and spatial arrangement stabilises the Cu$_3$(μ$_3$-X)(μ-X)$_2$ framework, the triangular Cu$_3$ core is approximately isosceles with one edge distance much longer than the other two as shown in Table 1. As no obvious direct Cu$\cdots$Cu bonding interactions[27] exist in these systems the Cu$\cdots$Cu distances were mainly determined

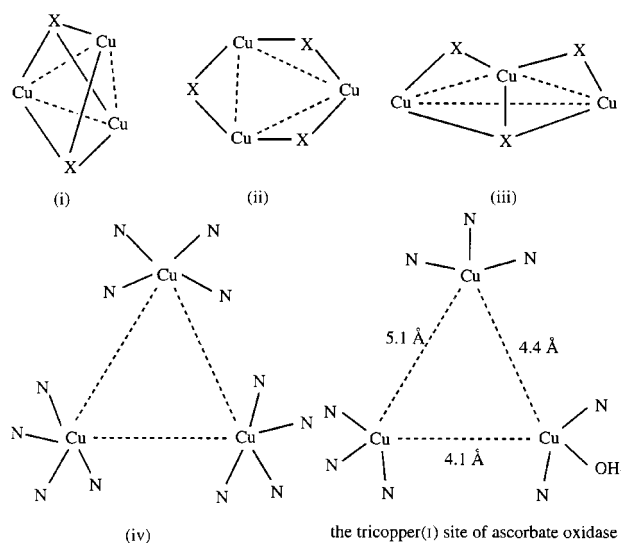**Fig. 2** Comparison of some triangular Cu$^I_3$ frameworks. (i) Ref. 8, (ii) ref. 25, (iii) this work, (iv) ref. 26. See text for detailed discussion

by the spatial arrangements and bridging length of the ligands and the electronic properties of the bridging anions. The Cu$\cdots$Cu distances in some of the trinuclear Cu$_3$ complexes are listed in Table 2. Besides the triangular Cu$_3$ frameworks shown in Fig. 2, equilateral triangular Cu$_3$ geometry linked by Cu–H–B and Cu–Cu interactions was found in [Cu$_3$(μ-H)$_3$-{C$_2$B$_9$H$_9$[C$_5$H$_4$N(CO$_2$CH$_3$)-4]}][28a] with a relatively short copper–copper distance of 2.519(2) Å. G. van Koten and co-workers[28c] reported two triangular organocopper(I) complexes bridged by aryl and O$_2$CPh in [Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(O$_2$CPh)$_2$], aryl and Br in [Cu$_3$Br{C$_6$H$_4$(CH$_2$MeCH$_2$CH$_2$NMe$_2$)-2}$_2$].

Solution studies

The electronic absorption spectrum of complexes **1**–**3** show bands at about 226 and 256 nm in dichloromethane, attributable to the intraligand transition of dpmt, since the unco-ordinated dpmt also absorbs strongly in this region. The low-energy absorptions at about 320 nm of **1** and 300 nm of **2** are likely to arise from a ligand-to-metal charge transfer (LMCT) transition. The room-temperature ^{31}P-{^{1}H} and ^{1}H NMR spectra of **1** show a singlet ^{31}P resonance at δ −16.9 and singlet thiophene proton resonances at δ 5.61 respectively, which means the surroundings of the two dpmt ligands around the trinuclear Cu$_3$(μ$_3$-I)(μ-I)$_2$ plane are identical. The existence of two sets of doublet methylene proton resonances at δ 4.12 (J = 14.0) and 3.61 (J = 14.0 Hz) indicates that the two geminal methylene protons are non-equivalent and are coupled to each other, so that rotation of bridging ligands around the trinuclear Cu$_3$(μ$_3$-I)(μ-I)$_2$ framework is blocked. The non-equivalence of the two methylene protons in the ^{1}H NMR spectrum arises on account of the different orientations of the two protons to the trinuclear Cu$_3$(μ$_3$-I)(μ-I)$_2$ framework, with one equatorial and the other axial which is also established in the solid structure of **1**. The ^{31}P-{^{1}H} and ^{1}H NMR spectra of **2** at room temperature (300 K) are similar to those of **1** in CDCl$_3$ solution, exhibiting a singlet ^{31}P resonance at δ −10.3, singlet thiophene proton resonances at δ 5.44 and two sets of doublets at δ 4.04 and 3.48, again indicating that the two ligands are symmetrically oriented with respect to the trinuclear Cu$_3$(μ$_3$-Br)(μ-Br)$_2$ framework. Additional weak resonances at δ 1.2 and −8.0 in ^{31}P-{^{1}H} NMR and δ 5.73 in ^{1}H NMR suggest that there is also a minor amount of another isomer in solution. Variable-temperature ^{31}P-{^{1}H} and ^{1}H NMR spectra of **2** are unchanged over the range 218 to 320 K. Those of the minor isomer exhibit some changes as evident in thiophene protons at δ 5.68 (320 K) to 5.85 and 5.79 (218 K) and several methylene proton resonances

Table 2 Comparison of Cu $\cdots$ Cu distances (Å) in some of the triangular Cu$_3$ frameworks

Complex	Cu $\cdots$ Cu			Ref
[Cu$_3$(μ_3-I)(μ-I)$_2$(μ-dpmt)$_2$]	2.857(2)	2.949(2)	5.104(3)	a
[Cu$_3$(μ_3-Br)(μ-Br)$_2$(μ-dpmt)$_2$]·2CH$_2$Cl$_2$	2.819(2)	2.885(2)	4.907(3)	a
[Cu$_3$(μ_3-Cl)(μ-Cl)$_2$(μ-dpmt)$_2$]·1.25CH$_2$Cl$_2$	2.832(2)	2.891(2)	4.648(3)	a
[Cu$_3$(μ_3-I)(μ-I)(μ-dppm)$_3$]	2.546(3)	2.916(4)	3.142(4)	8(b)
[Cu$_3$(μ_3-Cl)(μ-dppm)$_2$]Cl	3.175(4)	3.175(4)	3.281(3)	8(a)
[Cu$_3$(μ_3-OH)(μ-dppm)$_3$][BF$_4$]$_2$	3.120(2)	3.127(2)	3.322(2)	8(c)
[Cu$_3$(μ_3-η^1-C≡CR)(μ-η^1-C≡CNR)(μ-dppm)$_3$][BF$_4$]	2.497(2)	2.800(2)	3.294(2)	8(i)^b
[Cu$_3$(μ_3-η^1-C≡CPh)(μ-dppm)$_3$][BF$_4$]$_2$	2.813(2)	2.904(3)	3.274(3)	8(d)
[Cu$_3$(μ_3-η^1-C≡CPh)$_2$(μ-dppm)$_3$][BF$_4$]	2.570(3)	2.598(3)	2.615(3)	8(d)
[Cu$_3$(μ_3-η^1-C≡CPh)(μ_3-Cl)(μ-dppm)$_3$][BF$_4$]	2.785(3)	2.803(3)	2.871(3)	8(d)
Na[Me$_3$NCH$_2$Ph]$_2$[Cu$_3$(S$_2$C$_2$H$_4$)$_3$]·MeOH	2.749(1)	2.751(1)	2.846(1)	25(d)
[{Cu[(PhO)$_2$P(S)NC(S)NEt$_2$]}$_3$]	2.769(1)	2.773(1)	2.816(1)	25(e)
[Cu$_3$(C$_6$H$_2$Me$_3$-2,4,6)(O$_2$CPh)$_2$]	2.421(2)	2.421(2)	2.888(2)	28(b)
[Cu$_3$Br{C$_6$H$_4$(CH$_2$MeCH$_2$CH$_2$NMe$_2$)-2}$_2$]	2.403(1)	2.409(1)	3.299(1)	28(c)
[Cu$_3$L$^1{}_2$][PF$_6$]^c	2.915	3.500	3.614	26(b)
[Cu(μ-L^2)$_2${Cu(cnge)(MeCN)}$_2$][BF$_4$]$_3$·MeCN^d	3.624(16)	3.634(15)	5.011(15)	26(a)
Tricopper(I) site of ascorbate oxidase	4.1	4.4	5.1	24

^{a} This work. ^{b} R = 4-MeC$_6$H$_4$. ^{c} L^1 = Hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate. ^{d} L^2 = 3,6-Bis(3-*tert*-butylpyrazolyl)pyridazine, cnge = 2-cyano-guanidine.

at 218 K, suggesting fluxional behaviour in solution. It is of interest that the relative concentration of the two isomers is dependent on the temperature. The minor : major concentration ratio is 0.08, 0.10, 0.18, 0.21 and 0.75 : 1 at 218, 233, 273, 300 and 320 K respectively, indicating that the higher the temperature the higher is the concentration of the minor isomer, and transformation of the major to the minor isomer is an endothermic reaction. The solid structure of **2** shows that the Cu(3)−Br(1) interaction is comparatively weak with a long bond distance of 2.79(1) Å, so there is a possible equilibrium (1)
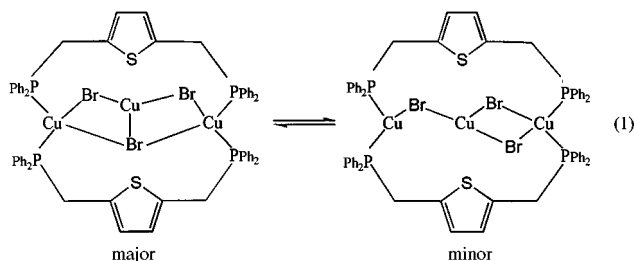
in CDCl$_3$ solution with $\Delta H^\ddagger$ *ca.* 6.5 kJ mol^{-1} obtained from the Van't Hoff equation.[29]

Room-temperature ^{31}P-{^{1}H} and ^{1}H NMR spectra of complex **3** in CDCl$_3$ solution, however, are quite different from those of **1** and **2**, and show two sets of singlet ^{31}P resonances at δ −2.5 and −7.4, one set of thiophene proton resonances at δ 5.70 and one set of methylene proton resonances at δ 3.71. Variable-temperature NMR spectroscopy was used to probe the dynamic behaviour of **3** in CDCl$_3$ solution as shown in Fig. 3. At ambient and sub-ambient temperatures, the ^{31}P-{^{1}H} NMR spectrum shows two singlet resonances. On increasing the temperature the two sets of singlet ^{31}P resonances gradually coalesce to a broad ^{31}P resonance at δ −2.9 with a coalescence temperature of 323 K. Likewise, at low temperatures, the ^{1}H NMR spectrum has two sets of singlet at δ 5.84 and 5.77 (218 K), which gradually coalesce to a singlet for thiophene protons at δ 5.70 (300 K) with a coalescence temperature of 286 K. At 218 K the ^{1}H NMR shows four sets of doublet methylene protons at δ 4.28 (^2J = 13.5), 3.70 (^2J = 13.7), 3.52 (^2J = 13.5) and 3.46 (^2J = 13.7 Hz). Irradiation of the protons at δ 3.70 removes the doublet coupling at δ 3.46, indicating they are coupled to each other; similarly, the protons at δ 4.28 are coupled with those at δ 3.52. The two sets of singlet ^{31}P resonances have an integration ratio of 1 : 0.92 at 218 K. The different NMR behaviour of **3**, compared with those of **1** and **2** in solution, possibly indicates that its structure in solution is different
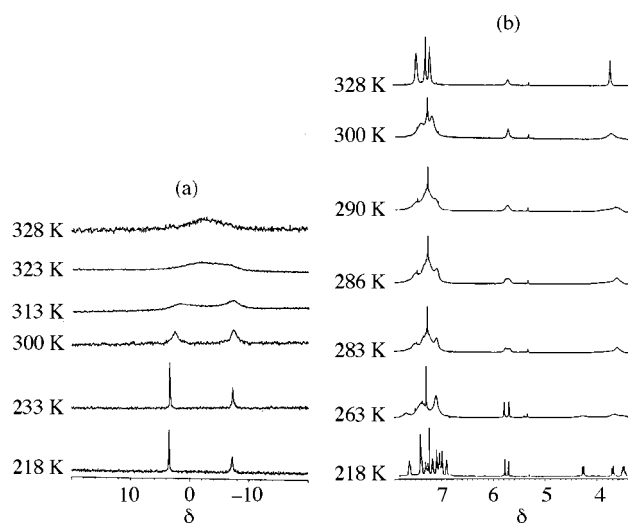
Fig. 3 Variable-temperature ^{31}P-{^{1}H} (a) and ^{1}H (b) NMR spectra of complex **3** in CDCl$_3$; the signals at δ *ca.* 5.30 in (b) are from CH$_2$Cl$_2$

from that in the solid phase. The molecular structure of **3** indicates that the Cu(3)−Cl(1) bond distance [2.757(2) Å] is very long and interaction between Cu(3) and Cl(1) is comparatively weak. The above NMR behaviour in solution suggests that **3** is undergoing the fluxional process shown in equation (2).
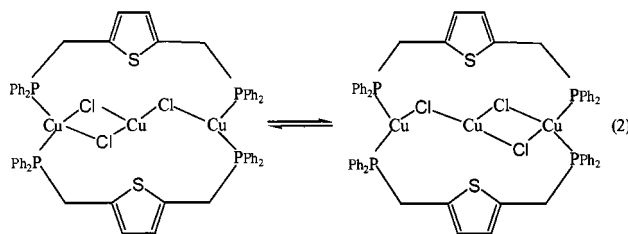
At high temperature, rapid equilibration leads to equivalence of four phosphorus atoms and only one set of ^{31}P-{^{1}H} signals can be resolved. Fluxional processes involving chlorine mobility have been established in NMR studies of some trinuclear complexes such as [Rh$_3$(CO)$_3$(μ-Cl)Cl(μ-dpmp)$_2$]BPh$_4$,[18a,c] [Ir$_3$-(μ-CO)$_2$(CO)$_2$(μ-Cl)Cl(μ-dpma)$_2$]BPh$_4$, [Ir$_2$Rh(μ-CO)$_2$(CO)$_3$-(μ-Cl)(μ-dpma)$_2$]BPh$_4$ and [Rh$_2$Pd(μ-Cl)(CO)$_2$Cl$_2$(μ-dpma)$_2$]-BPh$_4$[30] {dpma = bis[(diphenylphosphino)methyl]phenylarsine}. The activation energy $\Delta G^\ddagger$ for process (2) calculated by the Eyring equation[31] is *ca.* 57 kJ mol^{-1} from VT ^{31}P-{^{1}H} NMR

Table 3 Crystal data and refinement details for complexes **1**, **2**·2CH₂Cl₂ and **3**·1.25CH₂Cl₂

	1	**2·2CH₂Cl₂**	**3·1.25CH₂Cl₂**
Formula	$C_{60}H_{52}Cu_3I_3P_4S_2$	$C_{62}H_{56}Br_3Cl_4Cu_3P_4S_2$	$C_{61.25}H_{54.5}Cl_{5.5}Cu_3P_4S_2$
M	1532.34	1561.22	1364.14
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a/Å	29.207(4)	58.950(6)	58.830(1)
b/Å	9.929(2)	10.390(2)	10.219(1)
c/Å	22.083(4)	21.589(3)	21.663(1)
β/°	110.78(1)	104.33(2)	104.00(1)
U/Å³	5987(2)	12 812(3)	12 636(1)
Z	4	8	8
D_c/mg cm⁻³	1.700	1.619	1.434
μ/mm⁻¹	2.816	3.229	1.438
$F(000)$	3000	6240	5556
Crystal size/mm	$0.33 \times 0.25 \times 0.23$	$0.30 \times 0.20 \times 0.13$	$0.50 \times 0.38 \times 0.25$
hkl Index ranges	−35 to 29, −9 to 11, −21 to 26	−57 to 71, −12 to 11, −24 to 26	−47 to 73, −12 to 11, −27 to 26
Independent reflections	10 820	11 775	12 811
No. parameters refined	649	703	703
Largest difference peak and hole/e Å⁻³	2.34, −1.70	2.69, −2.36	1.62, −1.41
$R1^a$ [$I > 2\sigma(I)$]	0.0713	0.0536	0.0685
$wR2^b$	0.1844	0.1449	0.1956
Goodness of fit on F^2	1.031	1.047	0.966

^{a} $R1 = \Sigma w|F_o - F_c|/\Sigma(F_o)$. ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$.

spectra ($T_c = 323$ K, $\Delta\nu = 2171$ Hz), agreeing well with a value of *ca.* 60 kJ mol⁻¹ derived from VT ¹H NMR spectra for the coalescence of thiophene protons ($T_c = 286$ K, $\Delta\nu = 34.3$ Hz). Variable-temperature ³¹P-{¹H} and ¹H NMR spectra of the minor isomer of **2** are similar to those of **3** in solution, indicating that the minor isomer of **2** also shows similar fluxional behaviour to that of **3**. The different NMR behaviours of complexes **1**–**3**, to some extent, are attributed to a size effect of the halide anions. The small size of chlorine (X = Cl) is not large enough for Cl(1) to make contact with all three copper centres, so that the Cu(2)–Cl(1) or Cu(3)–Cl(1) bond is readily broken in solution.

Experimental

Materials and methods

All solvents were dried and degassed prior to use and all reactions were carried out under a nitrogen atmosphere. Elemental analyses were carried out by the Microanalytical Laboratory of the Department of Chemistry, National University of Singapore. Electron impact mass spectra were recorded on a Micromass VG 7035 mass spectrometer at 70 eV (*ca.* 1.12×10^{-17} J), UV/VIS spectra at room temperature on a Shimadzu UV-240 spectrophotometer in CH₂Cl₂ solution and NMR spectra on a Bruker AC500 at 500.14 (¹H) or 202.46 MHz (³¹P) using SiMe₄ or 85% H₃PO₄ as standards. The compounds 2,5-bis(chloromethyl)thiophene,[32] PPh₂H[33] and [Cu(MeCN)₄]-PF₆[34] were prepared according to the published methods. Other reagents were used as received.

Preparations

2,5-Bis[(diphenylphosphino)methyl]thiophene. A solution of LiPPh₂ (45.0 mmol) in thf (150 cm³) was prepared from PPh₂H (7.9 cm³, 45.0 mmol) and LiBuⁿ in hexane (1.6 M, 28.1 cm³, 45.0 mmol) and cooled to 0 °C. To this solution was slowly added freshly distilled 2,5-bis(chloromethyl)thiophene (22.5 mmol, 4.08 g) dissolved in thf (150 cm³). The solution was stirred for 3 h at room temperature, after which the thf was removed under vacuum. The residue was dissolved in dichloromethane (150 cm³), and the solution washed with water (3 × 150 cm³). After removing the solvent, crystallisation of the residue from methanol gave 4.76 g (44%) of dpmt as pale yellow crystals.

δ(³¹P) −11.2 (s); δ(¹H) 7.60–7.34 (m, 20 H, phenyl ring), 6.36 (s, 2 H, thiophene ring) and 3.48 (s, 4 H, methylene). EI MS: *m/z* 480 (M^+) (Found: C, 74.85; H, 5.38; S, 6.46. Calc. for C₃₀H₂₆P₂S: C, 74.96; H, 5.45; S, 6.67%).

2,5-Bis(diphenylphosphorylmethyl)thiophene. A dichloromethane solution (20 cm³) of dpmt (1 mmol, 0.48 g) was gently heated for 5 min. After removing the solvent *in vacuo*, crystallisation of the residue from dichloromethane–acetonitrile gave 0.38 g (75%) of colourless crystals. δ(³¹P) 28.4 (s); δ(¹H) 7.69–7.40 (m, 20 H), 6.57 (d, 2 H) and 3.72 [d, 4 H, ³*J*(PH) = 12.4 Hz]. EI MS: *m/z* 512 (M^+) (Found: C, 70.20; H, 5.01; S, 6.18. Calc. for C₃₀H₂₆O₂P₂S: C, 70.28; H, 5.11; S, 6.25%).

[Cu₃(μ₃-X)(μ-X)₂(μ-dpmt)₂] (X = I 1 or Br 2). The compound dpmt (0.30 mmol) was added to a stirred solution of [Cu-(MeCN)₄]PF₆ (0.45 mmol) in acetonitrile (15 cm³). After 2 h, methanol (10 cm³) containing KX (0.90 mmol) was added and stirred for 1 h. The precipitated white powder was collected and recrystallised from CH₂Cl₂–MeOH in 45–58% yield. Compound **1**: δ(³¹P) (CDCl₃, 298 K) −16.9 (s); δ(¹H) (CDCl₃, 298 K) 8.61–6.90 (m, 20 H), 5.61 (s, 2 H), 4.12 [d, 2 H, ²*J*(HH) = 14.0] and 3.61 [d, 2 H, ²*J*(HH) = 14.0 Hz]; UV/VIS λ_{max}/nm (ε/M⁻¹ cm⁻¹) 226 (88 200), 256 (sh, 54 100) and 320 (sh, 12 200) (Found: C, 47.15; H, 3.46; Cu, 11.86; S, 4.32. Calc. for C₆₀H₅₂Cu₃I₃P₄S₂: C, 47.02; H, 3.42; Cu, 12.44; S, 4.18%). Compound **2**: δ(³¹P) (CDCl₃, 300 K) −10.3 (s); δ(¹H) (CDCl₃, 300 K) 7.72–6.87 (m, 20 H), 5.44 (s, 2 H), 4.04 [d, 2 H, ²*J*(HH) = 13.6] and 3.48 [d, 2 H, ²*J*(HH) = 13.4 Hz]; UV/VIS λ_{max}/nm (ε/M⁻¹ cm⁻¹) 226 (89 300), 256 (sh, 61 200) and 300 (sh, 24 500) (Found: C, 51.49; H, 3.58; Cu, 13.14; S, 4.25. Calc. for C₆₀H₅₂Br₃Cu₃P₄S₂: C, 51.78; H, 3.77; Cu, 13.71; S, 4.61%).

[Cu₃(μ₃-Cl)(μ-Cl)₂(μ-dpmt)₂] 3. Compound dpmt (0.30 mmol) was added to a stirred solution of [Cu(MeCN)₄]PF₆ (0.45 mmol) in acetonitrile (15 cm³). After 2 h an aqueous solution (10 cm³) containing NaCl (0.90 mmol) was added and stirred for 1 h. After the acetonitrile was removed *in vacuo*, CH₂Cl₂ (30 cm³), was added to the residue. The CH₂Cl₂ phase was washed twice with water (20 cm³) and evaporated to give crude complex **3**. This was purified by washing with small amounts of methanol and recrystallisation from CH₂Cl₂–MeOH to get **3** in 35% yield. δ(³¹P) (CDCl₃, 300 K) −2.5 (s) and −7.4 (s); δ(¹H)

(CDCl$_3$, 300 K) 7.37 and 7.17 (br, 20 H), 5.70 (s, 2 H) and 3.71 (s, 4 H). UV/VIS: λ_{max}/nm (ε/M^{-1} cm^{-1}) 226 (88 300) and 256 (sh, 53 600) (Found: C, 56.93; H, 4.46; Cu, 14.68; S, 4.85. Calc. for C$_{60}$H$_{52}$Cl$_3$Cu$_3$P$_4$S$_2$: C, 57.27; H, 4.17; Cu, 15.16; S, 5.10%).

Crystallography

A single crystal of complex **1** was mounted on a glass fiber and covered with a film of an inert oil, while crystals of **2** and **3** were sealed into glass capillaries with the mother-liquor. Crystal data and a summary of the crystallographic analyses are given in Table 3. The data were collected at 295 K on a Siemens CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 73$ Å). All the structures were solved by direct methods and some non-hydrogen atoms located from Fourier-difference maps. All non-hydrogen atoms were refined anisotropically. Refinement was by full-matrix least squares based on F^2 using SHELXL 93.[35] Hydrogen atoms were placed in assigned positions and with their isotropic thermal parameters riding on the parent carbon atoms. The largest residual peaks and holes were found above and below the Cu$_3$(μ_3-X)(μ-X)$_2$ plane.

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