Copper(I) Complexes with 4,6-Dimethylpyrimidine-2-thione (Hdmpymt); the Crystal and Molecular Structure of $[Cu_6(dmpymt)_6]$†

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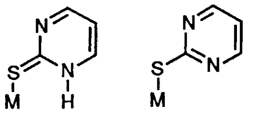
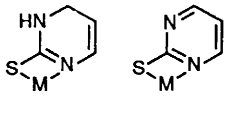
The complex $[Cu_6(dmpymt)_6]\cdot H_2O$ was synthesised by electrochemical oxidation of copper in an acetonitrile solution of the neutral ligand 4,6-dimethylpyrimidine-2-thione (Hdmpymt). The reaction of $[Cu_6(dmpymt)_6]$ with 1,2-bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)-ethane (dppe) yielded compounds of general formulae [Cu(dmpymt)(dppm)] and $[Cu_2(dmpymt)_2(dppe)_3]$. The molecular structure of $[Cu_6(dmpymt)_6]$ was determined: the crystals are triclinic, space group $P1$, $a = 11.432(3)$, $b = 13.395(2)$, $c = 15.694(4)$ Å, $\alpha = 80.28(2)$, $\beta = 87.75(2)$, $\gamma = 73.87(2)°$ and $Z = 2$. The six copper atoms are arranged with distorted-octahedral geometry, each copper atom being trigonally co-ordinated to one nitrogen and two sulfur atoms of three different ligands. Infrared, ^1H, ^{13}C and ^{31}P NMR spectral data are presented for all the compounds.

One of the main reasons for the current interest in copper-sulfur compounds[1] is that they can be used as models for copper–cysteine centres in metalloproteins such as plastocyanin and azurin.[2] Although complexes of copper with pyridine-2-thione have been studied,[3,4] there is a paucity of data on complexes with pyrimidine-2-thione, a heterocyclic thione base with analogous tautomerism of the type $-NH-C{=}S \longleftrightarrow -N{=}C-SH$.[5] We report here the synthesis and properties of the complex of 4,6-dimethylpyrimidine-2-thione (Hdmpymt) with copper and of its adducts with 1,2-bis(diphenylphosphino)-methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe). Pyrimidine-2-thione is known to be able to act as a monodentate ligand through the sulfur atom[6] (**A**), as a chelating ligand[7] (**B**) and as a bridging ligand through its nitrogen and sulfur atoms[8] (**C**); $[Cu_6(dmpymt)_6]$ is the first reported complex in which pyrimidine-2-thione links three metal atoms (**D**).



A



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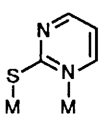
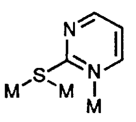


C



D

Experimental

Solvents, 4,6-dimethylpyrimidine-2-thione, 1,2-bis(diphenyl-phosphino)methane, 1,2-bis(diphenylphosphino)ethane and other reagents were all commercial products used without further purification. Copper (Ega Chemie) was used as plates (*ca.* 2 × 2 cm).

Preparation of Complexes.—$[Cu_6(dmpymt)_6]$. The electrochemical method used in the synthesis of the compound was similar to that described by Tuck and co-workers.[9] A copper anode was oxidized electrochemically in a solution of 4,6-dimethylpyrimidine-2-thione (0.1569 g, 1.121 mmol) and tetraethylammonium perchlorate (20 mg) as supporting electrolyte in MeCN (50 cm^3) using a platinum cathode and an applied voltage of 26 V (current 10 mA). A yellow precipitate formed immediately at the anode and hydrogen was evolved at the cathode. The solid was collected and dissolved in $CHCl_3$, the solution was filtered to remove any solid impurities, and the filtrate was left to concentrate by evaporation at room temperature. The compound obtained was identified as $[Cu_6(dmpymt)_6]\cdot H_2O$ (Found: C, 35.2; H, 3.4; N, 13.4. Calc. for $C_{36}H_{44}Cu_6N_{12}OS_6$: C, 35.0; H, 3.6; N, 13.6%). The electrochemical efficiency, was 0.98 mol F^{-1}. The cell used can be summarized as Pt(−)|MeCN + Hdmpymt|Cu(+).

[Cu(dmpymt)(dppm)]. A solution of dppm (0.09 g, 0.2289 mmol) in acetone–CH_2Cl_2 (4:3, 7 cm^3) was added to a suspension of $[Cu_6(dmpymt)_6]$ (0.0309 g, 0.1526 mmol) in acetone (4 cm^3). The mixture was refluxed for 1 h, and the resulting solution was treated with hexane. The yellow solid precipitated was identified as [Cu(dmpymt)(dppm)] [Found: C, 63.4; H, 4.8; N, 4.6; *M*, 950. Calc. for $C_{31}H_{29}CuN_2P_2S$: C, 63.4; H, 4.8; N, 4.9; 1174.3 (for dimer)].

$[Cu_2(dmpymt)_2(dppe)_3]$. To a suspension of $[Cu_6(dmpymt)_6]$ (0.1192 g, 0.59 mmol) in acetone (5 cm^3) was added a solution of dppe (0.35 g, 0.86 mmol) in the same solvent (40 cm^3). The reaction mixture was refluxed until a clear solution was obtained; concentration at room temperature afforded a yellow solid identified as $[Cu_2(dmpymt)_2(dppe)_3]$ (Found: C, 67.5; H, 5.7; N, 3.7; *M*, 1592. $C_{90}H_{86}Cu_2N_4P_6S_2$: C, 67.5; H, 5.4; N, 3.5%; *M*, 1600.7).

Attempts were made to prepare other mixed-ligand complexes (*a*) by the electrochemical technique, adding nitrogen-containing ligands such as pyridine, 1,10-phenanthroline or 2,2′-bipyridine to the Hdmpymt solution, and (*b*) by reaction

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

between these bases and [Cu_6(dmpymt)$_6$] in 1,2-dichloromethane and acetone as solvents. These experiments were unsuccessful, the compounds isolated still having the elemental formula of [Cu(dmpymt)].

Physical Measurements.—Microanalyses were performed using a Carlo-Erba EA1108 microanalyser. Infrared spectra were recorded in KBr mulls on a Perkin-Elmer 180 spectrophotometer, ^1H, ^{13}C and ^{31}P NMR spectra on a Bruker WM 250 MHz instrument using $CDCl_3$ as solvent. Molecular weights were determined in $CHCl_3$ using a Knauer osmometer.

Crystal Structure Determination.—*Crystal data.* $C_{36}H_{42}Cu_6N_{12}S_6 \cdot H_2O$, $M = 1234.46$, triclinic, space group $P1$, $a = 11.432(2)$, $b = 13.395(2)$, $c = 15.694(4)$ Å, $\alpha = 80.28(2)$, $\beta = 87.75(2)$, $\gamma = 73.87(2)^\circ$, $U = 2275(1)$ Å^3 (by least-squares refinement of diffractometer angles for 22 automatically centred reflections, $8 < \theta < 19^\circ$, $\lambda = 0.7103$ Å), $Z = 2$, $D_c = 1.521$ g cm^{-3}, $F(000) = 1244$. Prismatic yellow crystal with dimensions 0.18 × 0.28 × 0.37 mm, μ(Mo-Kα) = 28.038 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω–2θ mode with scan width = $0.85 + 0.35\tan\theta$, graphite-monochromated Mo-Kα radiation, 5842 reflections measured ($0 < \theta < 24^\circ$; $-11 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 14$, $0 \leqslant l \leqslant 17$), 5571 unique (merging $R = 0.020$), 3545 with $I \geqslant 3\sigma(I)$; Lorentz and polarization corrections. Absorption corrections were applied at a later stage in the refinement[10] (maximum, minimum transmission factors = 1.131, 0.906). The intensity of one standard reflection was essentially constant throughout data collection.

Structure analysis and refinement. Standard direct methods followed by normal Fourier difference techniques. Blocked-matrix least-squares refinement with all non-H atoms anisotropic, and hydrogens included, as fixed contributors, were those found in difference maps with two overall isotropic thermal parameters one for each independent molecule, which refined to $U_{iso} = 0.080$ and 0.085 Å^2 for molecule 1 and 2 respectively. The function minimized, $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$, gave satisfactory agreement. Final $R[=\Sigma|F_o| - |F_c|/\Sigma|F_o|$ and $R'\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ values were 0.044 and 0.041 respectively. Programs used: SHELX 86[11] and ORTEP.[12] Scattering factors for non-H atoms from Cromer and Mann[13] with corrections for anomalous dispersion from Cromer and Liberman,[14] for H from Stewart, *et al.*[15]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

Results and Discussion

The electrochemical oxidation of copper in an acetonitrile solution of 4,6-dimethylpyrimidine-2-thione (Hdmpymt) led to a compound of empirical formula [Cu(dmpymt)]. The electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, is close to 1 mol F^{-1}, which is compatible with the scheme in equations (1) and (2).

$$\text{Cathode: Hdmpymt} + e^- \longrightarrow \tfrac{1}{2}H_2(g) + \text{dmpymt}^- \quad (1)$$

$$\text{Anode: dmpymt}^- + \text{Cu} \longrightarrow [\text{Cu(dmpymt)}] + e^- \quad (2)$$

In order to understand the nature of [Cu(dmpymt)], crystals were grown from acetonitrile and an X-ray crystallographic analysis carried out. This showed that the compound was in fact [Cu_6(dmpymt)$_6$]. The unit cell contains two independent molecules of the complex and two molecules of water. The molecular structure of [Cu_6(dmpymt)$_6$] is shown in Fig. 1, together with the atomic numbering scheme adopted. Final atomic coordinates, selected bond distances and angles are listed in Tables 1 and 2. Each molecule of the unit cell has a symmetry centre coinciding with a crystallographic centre and can best be described as based on a distorted-octahedral core of six copper atoms. The two molecules are slightly different: one

Table 1 Final fractional atomic coordinates for [Cu_6(dmpymt)$_6$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cu(11)	0.4636(1)	0.0862(1)	0.1054(1)
Cu(12)	0.6762(1)	0.0429(1)	0.0121(1)
Cu(13)	0.5465(1)	−0.1255(1)	0.1136(1)
S(11)	0.4386(2)	0.2209(2)	−0.0044(2)
N(111)	0.6792(8)	0.1953(6)	−0.0170(5)
N(112)	0.5497(7)	0.3687(6)	−0.0587(6)
C(111)	0.780(1)	0.2289(9)	−0.0423(7)
C(112)	0.764(1)	0.3337(9)	−0.0751(7)
C(113)	0.647(1)	0.4037(8)	−0.0846(7)
C(114)	0.5681(9)	0.2667(8)	−0.0268(6)
C(115)	0.8994(9)	0.1484(9)	−0.0294(8)
C(116)	0.619(1)	0.5169(8)	−0.1202(9)
S(12)	0.2921(2)	0.0343(2)	0.1086(2)
N(121)	0.4134(7)	−0.1531(6)	0.1952(5)
N(122)	0.2018(7)	−0.0908(6)	0.2245(5)
C(121)	0.4191(9)	−0.2432(8)	0.2491(6)
C(122)	0.3156(9)	−0.2601(8)	0.2910(7)
C(123)	0.207(1)	−0.1813(8)	0.2785(7)
C(124)	0.3046(9)	−0.0804(8)	0.1853(6)
C(125)	0.5432(9)	−0.3209(8)	0.2614(7)
C(126)	0.0920(9)	−0.1937(9)	0.3207(8)
S(13)	0.7115(2)	−0.0736(2)	0.1327(2)
N(131)	0.5620(7)	0.0706(6)	0.2131(5)
N(132)	0.7590(7)	−0.0113(6)	0.2744(5)
C(131)	0.530(1)	0.1262(8)	0.2789(7)
C(132)	0.612(1)	0.1117(9)	0.3438(7)
C(133)	0.726(1)	0.0437(9)	0.3401(7)
C(134)	0.6734(9)	0.0028(7)	0.2148(6)
C(135)	0.4034(9)	0.2041(9)	0.2740(8)
C(136)	0.822(1)	0.028(1)	0.4073(8)
Cu(21)	0.1836(1)	0.4789(1)	0.4702(1)
Cu(22)	0.0412(1)	0.3505(1)	0.4619(1)
Cu(23)	0.0754(1)	0.4245(1)	0.6222(1)
S(21)	0.1196(2)	0.5257(2)	0.3314(2)
N(211)	0.0943(7)	0.3331(6)	0.3391(5)
N(212)	0.1164(7)	0.4270(6)	0.2000(5)
C(211)	0.0856(8)	0.2489(9)	0.3038(7)
C(212)	0.0903(9)	0.2569(9)	0.2138(8)
C(213)	0.1044(9)	0.3460(9)	0.1624(7)
C(214)	0.1111(8)	0.4174(7)	0.2849(6)
C(215)	0.070(1)	0.1541(8)	0.3636(8)
C(216)	0.104(1)	0.358(1)	0.0661(7)
S(22)	0.1649(2)	0.6184(2)	0.5376(2)
N(221)	0.2347(7)	0.6481(6)	0.6882(5)
N(222)	0.1683(6)	0.4937(6)	0.6902(5)
C(221)	0.2489(9)	0.6241(9)	0.7756(7)
C(222)	0.2267(9)	0.5349(9)	0.8201(6)
C(223)	0.1848(8)	0.4685(8)	0.7766(6)
C(224)	0.1944(8)	0.5828(7)	0.6492(6)
C(225)	0.285(1)	0.7043(9)	0.8181(7)
C(226)	0.1503(9)	0.3721(8)	0.8213(6)
S(23)	0.1541(2)	0.2710(2)	0.5787(2)
N(231)	0.3897(7)	0.1751(6)	0.5804(5)
N(232)	0.3285(7)	0.3493(6)	0.5001(5)
C(231)	0.5058(9)	0.1729(8)	0.5624(6)
C(232)	0.5383(9)	0.2564(9)	0.5132(7)
C(233)	0.4459(9)	0.3457(8)	0.4789(6)
C(234)	0.3065(9)	0.2662(8)	0.5497(6)
C(235)	0.5965(9)	0.0719(8)	0.5990(7)
C(236)	0.4679(9)	0.4342(9)	0.4171(7)
OW	−0.0356(7)	0.0582(7)	0.1861(6)

Table 2 Selected interatomic distances (Å) and angles (°) for [Cu_6(dmpymt)$_6$]

Molecule 1			
Cu(11)–Cu(12)	2.759(2)	Cu(11)–Cu(13)	2.711(2)
Cu(11)–S(11)	2.238(3)	Cu(11)–S(12)	2.251(3)
Cu(11)–N(131)	2.016(8)	Cu(12)–N(111)	2.025(8)
Cu(12)–S(13)	2.212(3)	Cu(12)–S(12^{I})	2.278(3)
Cu(13)–N(121)	2.023(8)	Cu(13)–S(13)	2.230(3)
Cu(13)–S(11^{I})	2.279(3)	S(11)–C(114)	1.76(1)
N(111)–C(111)	1.37(1)	N(111)–C(114)	1.36(1)
N(112)–C(113)	1.35(1)	N(112)–C(114)	1.33(1)
S(12)–C(124)	1.76(1)	N(121)–C(121)	1.34(1)
N(121)–C(124)	1.35(1)	N(122)–C(123)	1.34(1)
N(122)–C(124)	1.34(1)	S(13)–C(134)	1.75(1)
N(131)–C(131)	1.35(1)	N(131)–C(134)	1.34(1)
N(132)–C(133)	1.35(1)	N(132)–C(134)	1.33(1)
Molecule 2			
Cu(21)–Cu(23)	2.726(2)	Cu(21)–S(21)	2.255(3)
Cu(21)–S(22)	2.255(3)	Cu(21)–N(232)	2.041(8)
Cu(22)–N(211)	2.029(8)	Cu(22)–S(23)	2.219(3)
Cu(22)–S(22^{II})	2.276(3)	Cu(23)–N(222)	2.024(8)
Cu(23)–S(23)	2.214(3)	Cu(23)–S(21^{II})	2.270(3)
S(21)–C(214)	1.76(1)	N(211)–C(211)	1.37(1)
N(211)–C(214)	1.35(1)	N(212)–C(213)	1.36(1)
N(212)–C(214)	1.32(1)	S(22)–C(224)	1.76(1)
N(221)–C(221)	1.36(1)	N(221)–C(224)	1.33(1)
N(222)–C(223)	1.35(1)	N(222)–C(224)	1.36(1)
S(23)–C(234)	1.77(1)	N(231)–C(231)	1.34(1)
N(231)–C(234)	1.35(1)	N(232)–C(233)	1.36(1)
N(232)–C(234)	1.33(1)		
Molecule 1			
Cu(12)–Cu(11)–Cu(13)	71.78(5)	Cu(12)–Cu(11)–S(11)	74.78(8)
Cu(12)–Cu(11)–S(12)	133.87(9)	Cu(12)–Cu(11)–N(131)	89.6(2)
Cu(13)–Cu(11)–S(11)	132.65(9)	Cu(13)–Cu(11)–S(12)	76.41(8)
Cu(13)–Cu(11)–N(131)	88.0(2)	S(11)–Cu(11)–S(12)	105.6(1)
S(11)–Cu(11)–N(131)	124.4(2)	S(12)–Cu(11)–N(131)	122.0(2)
Cu(11)–Cu(12)–N(111)	94.5(2)	Cu(11)–Cu(12)–S(13)	74.35(8)
Cu(11)–Cu(12)–S(12)	126.49(9)	N(111)–Cu(12)–S(13)	133.0(2)
N(111)–Cu(12)–S(12)	110.6(2)	S(13)–Cu(12)–S(12)	112.6(1)
Cu(11)–Cu(13)–N(121)	93.1(2)	Cu(11)–Cu(13)–S(13)	75.09(8)
Cu(11)–Cu(13)–S(11)	128.23(9)	N(121)–Cu(13)–S(13)	132.1(2)
N(121)–Cu(13)–S(11)	109.2(2)	S(13)–Cu(13)–S(11)	114.5(1)
Molecule 2			
Cu(22)–Cu(21)–Cu(23)	65.46(5)	Cu(22)–Cu(21)–S(21)	78.38(8)
Cu(22)–Cu(21)–S(22)	133.19(9)	Cu(22)–Cu(21)–N(232)	89.1(2)
Cu(23)–Cu(21)–S(21)	133.84(9)	Cu(23)–Cu(21)–S(22)	77.05(8)
Cu(23)–Cu(21)–N(232)	90.3(2)	S(21)–Cu(21)–S(22)	112.9(1)
S(21)–Cu(21)–N(232)	117.8(2)	S(22)–Cu(21)–N(232)	119.1(2)
Cu(21)–Cu(22)–N(211)	91.7(2)	Cu(21)–Cu(22)–S(23)	77.69(8)
Cu(21)–Cu(22)–S(22)	131.36(9)	N(211)–Cu(22)–S(23)	124.4(2)
N(211)–Cu(22)–S(22)	106.0(2)	S(23)–Cu(22)–S(22)	121.9(1)
Cu(21)–Cu(23)–N(222)	93.2(3)	Cu(21)–Cu(23)–S(23)	77.13(8)
Cu(21)–Cu(23)–S(21)	132.29(9)	N(222)–Cu(23)–S(23)	124.3(2)
N(222)–Cu(23)–S(21)	104.9(2)	S(23)–Cu(23)–S(21)	122.2(1)

N(122) · · · OW	2.90(1)
OW · · · H(OW)	1.080(9)
N(122) · · · H(OW) · · · OW	121.4(5)
N(122) · · · H(OW)	2.189(8)

Symmetry operations: I, $1 - x, -y, -z$; II, $-x, 1 - y, 1 - z$.

has Cu–Cu–Cu angles in the range 48.62(5)–93.43(5)° and dihedral angles between pairs of the planes Cu(11)–Cu(12^{I})–Cu(11^{I})–Cu(12) (1), Cu(11)–Cu(13^{I})–Cu(11^{I})–Cu(13) (2) and Cu(12)–Cu(13^{I})–Cu(12^{I})–Cu(13) (3) of 94.65(2) for 1–2, 103.41(2) for 1–3 and 76.83(2)° for 2–3; in the other the range of Cu–Cu–Cu angles is 51.42(5)–90.70(5)° and the dihedral angles are 89.68(2), 81.38(2) and 99.77(2)°.

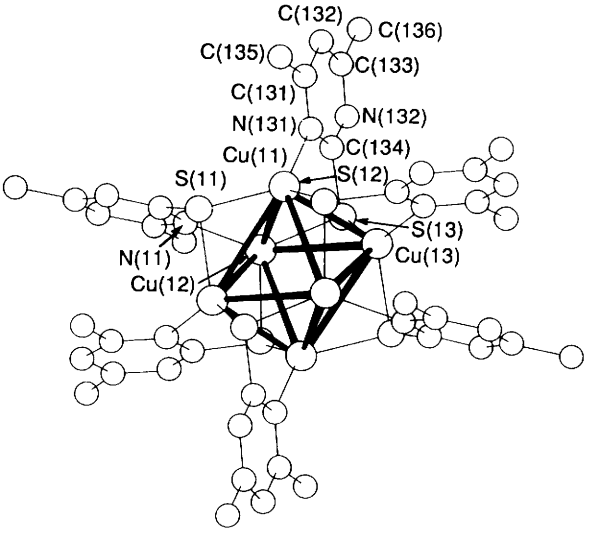

Fig. 1 Schematic view of the structure of [Cu_6(dmpymt)$_6$] showing the geometry of the octahedral Cu_6 core

The distances between copper atoms lie in two groups, one in the range 2.711(2)–2.759(2) Å and the other in the range 2.932(2)–3.433(2) Å; all these distances are considerably greater than the Cu–Cu distance in metallic copper (2.40 Å),[16] showing that no significant copper–copper interactions exist in the compound. Each ligand links the three copper atoms defining one of the faces of the octahedral core, being bound to one through one of the nitrogen atoms and to the other two through the sulfur atom. Two opposite faces of the octahedron are left exposed. Each copper is bound to three pyrimidine-2-thionate ligands (to two *via* sulfur atoms and to one *via* a nitrogen atom), and has distorted trigonal CuS_2N co-ordination being nearly 0.4 Å from the plane formed by the donor atoms [see the co-ordination around Cu(11) in Fig. 1]. Each bridging sulfur atom has one Cu–S bond slightly longer than the other but neither [range 2.212(3)–2.279(3) Å] differs significantly in length from the average Cu–S distance observed in pyridine-2-thionate copper complexes such as [$Cu_6(C_5H_4NS)_6$][4] [2.238(2) Å] and [$Cu_6(C_5H_3NSSiMe_3)_6$][3] [2.245(2) Å] which are also hexanuclear copper(I) complexes with trigonal geometry about each metal centre. The Cu–N distances (mean 2.022 Å) are likewise similar to those observed in the above-mentioned pyridine-2-thionate copper(I) complexes, 2.034(7) and 2.030(7) Å respectively. The bond angles around the copper atom show distorted-trigonal geometry, with S–Cu–S and S–Cu–N in the ranges 105.6(1)–122.2(1) and 106.0(2)–133.0(2)° respectively. The pyrimidine rings are essentially planar, with the sulfur atoms lying approximately in the plane of the pyrimidine ring to which they are bound. The average S–C and C–N bond distances of 1.76(1) and 1.35(1) Å are similar to those found in other pyrimidine-2-thionate complexes, indicating that the N–C bond order is *ca.* 1.5 and that the ligand is co-ordinated in a form that is closer to pyrimidine-2-thionate than to the thione form.[17]

There is evidence for a weak hydrogen bond between the water molecules of the crystal and the nitrogen atom that is not co-ordinated to the pyrimidine-2-thionate ligand. The only short distances are O–H · · · N [2.90(1) Å] and H · · · N [2.189(8) Å], with an associated O–H · · · N angle of 121.4(5)°. The distances are less than the sums of the van der Waals radii of O and N (3.07 Å) and H and N (2.75 Å), but significantly greater than these expected for a strong hydrogen bond, 2.78 and 1.78 Å respectively.[18]

The reaction of [Cu_6(dmpymt)$_6$] and excess of 1,2-bis(diphenylphosphino)methane or 1,2-bis(diphenylphosphino)ethane in acetone or acetone–CH_2Cl_2 as solvent afforded the products [Cu(dmpymt)(dppm)] and [Cu_2(dmpymt)$_2$(dppe)$_3$]. The infrared spectra of the compounds show no bands assignable to ν(N–H) (3200–3050 cm^{-1} for the free ligand),[19]

Table 3 Proton NMR data for the complexes *

	Pyrimidine ligand			Phosphines	
Compound	NH	H(5)	H(4′),H(6′)	Aromatic	CH_2
Hdmpymt	13.49 (br)	6.47 (s, 1)	2.43 (s, 6)		
[{Cu(dmpymt)}$_6$]		6.68 (s, 1)	2.52 (s, 3) 2.40 (s, 3)		
dppm				7.59–7.27 (m, 10)	2.81(1)
[Cu(dmpymt)(dppm)]		6.70 (s, 1)	2.40 (s, 6)	7.72–6.92 (m, 30)	3.22 (br, 2)
dppe				7.34–7.26 (m, 5)	2.10 (t, 1)
[Cu_2(dmpymt)$_2$(dppe)$_3$]		6.20 (s, 1)	2.29 (br, 6)	7.70–7.09 (m, 30)	1.99 (s, 4) 2.52 (s, 2)

* Integrated relative intensities in parentheses, H(4′) and H(6′) are methyl hydrogens.

Table 4 Carbon-13 and ^{31}P NMR data for the complexes *

	Pyrimidine ligand				Phosphines		
Compound	C(2)	C(4),C(6)	C(5)	C(4′),C(6′)	Aromatic	CH_2	^{31}P
Hdmpymt	180.52	164.97	111.05	21.76			
[{Cu(dmpymt)}$_6$]	176.75	167.66 165.58	115.15	24.41 24.00			
dppm					138.82, 132.88, 128.73	29.97 (t)	−22.00
[Cu(dmpymt)(dppm)]	167.80	162.40	115.80	18.35	132.60, 130.03, 128.51	23.75	−16.54
dppe					138.17, 132.77, 128.70	23.77	−12.52
[Cu_2(dmpymt)$_2$(dppe)$_3$]	164.70		111.72	23.13	135.32, 130.91, 128.52	29.63 (m) 25.09 (m)	−9.19 +31.22

* Atoms C(4′) and C(6′) are methyl carbons.

suggesting that deprotonation of the NH group has occurred, and therefore that the ligand is co-ordinated in thionate form. In addition, the phosphine complexes exhibit the expected bands due to the dppm or dppe ligand.[20] For [Cu(dmpymt)(dppm)] these occur at 1480m, 1384w, 1190mw, 1100s, 1030m, 1000m, 785m, 735s and 700vs cm^{-1}. For [Cu_2(dmpymt)$_2$(dppe)$_3$] the ligand bands are found at 1480m, 1330w, 1160m, 1025m, 1005m, 750s, 730s and 705vs cm^{-1}.

The ^1H NMR spectra (Table 3) of all the complexes at room temperature show that the broad NH singlet of the free ligand at about δ 13.49 is absent. The ^{13}C NMR spectra (Table 4) show the signals of the carbons of the dmpymt$^-$ ligand, with the signal attributable to C(2) shifted towards higher field than for the free ligand, suggesting that dmpymt$^-$ has a greater contribution from the thionate form in the complexes.[21]

The ^1H NMR spectrum of [Cu_6(dmpymt)$_6$] exhibits a singlet at δ 6.68 attributed to the CH of dmpymt$^-$, and two signals at about δ 2.52 and 2.40 for the methyl protons of dmpymt$^-$. Thus the two methyl groups are non-equivalent, which is in keeping with the bidentate character of 4,6-dimethylpyrimidine-2-thionate shown in this complex by the X-ray diffraction data. These results show that in solution the complex retains the structure observed in the solid state. The ^{13}C NMR spectrum is consistent with these data and exhibits two signals at δ 24.41 and 24.00 attributable to the non-equivalent C′(4) and C′(6) of the methyl groups.

The ^1H NMR spectrum of the complex [Cu(dmpymt)(dppm)] exhibits a multiplet in the aromatic region and a singlet at δ 3.22 that are attributable to the phenyl and methylene protons of the dppm ligand, respectively. In addition, a single signal due to the methyl hydrogens of the dmpymt$^-$ ligand is observed, suggesting that the two methyl groups are chemically equivalent. This equivalence can also be seen in the ^{13}C NMR spectrum in which a single signal assignable to the methyl carbon atoms is observed. This behaviour may be due either to the pyrimidine-2-thione acting in a monodentate manner through the sulfur atom, or to fluxional behaviour if it acts as a chelating ligand. It is tentatively suggested that the former is the case because the ^1H NMR spectrum does not change with temperature, and at 213 K the methyl hydrogens give a single signal. The ^{13}C NMR spectrum of this compound has a complex set of resonances in the aromatic region δ 132.6–128.5 and a signal at δ 23.75, the former assignable to the phenyl carbons of dppm and the latter to its methylene carbons. The ^{31}P NMR spectrum in $CDCl_3$ as a singlet at δ −16.5 (relative to external 85% H_3PO_4) that has shifted from δ −22.00 for dppm itself in the same solvent. This shows that all the phosphorus atoms are equivalent, the downfield shift indicating that in this compound dppm acts as a bridging ligand.[22] We therefore suggest that the complex [Cu(dmpymt)(dppm)] probably has a dimer structure with trigonal co-ordination for each copper, as found for [Cu_2{$OC_6Cl_4(OH)$}$_2$(dppm)$_2$] [$C_6Cl_4(OH)_2$ = tetrachloro-1,2-dihydroxybenzene] by X-ray diffraction.[23] This dimeric structure is in accordance with the value of the molecular weight determined in $CHCl_3$.

The ^1H NMR spectrum of the complex [Cu_2(dmpymt)$_2$(dppe)$_3$] has a multiplet at about δ 7.70–7.09 due to the phenyl hydrogens of dppe. In addition, two signals due to the dppe methylene hydrogens appear at δ 1.99 and 2.52 with intensities in the ratio 2:1, suggesting the presence of two non-equivalent dppe ligands in this compound. This spectrum also shows a singlet at δ 6.20 and a broad signal at δ 2.29 that are attributable to the H(5) and methyl protons of dmpymt$^-$ respectively. The low-temperature ^1H NMR spectrum shows that at 213 K the equivalence of the methyl protons is maintained. The ^{13}C NMR spectrum shows resonances in the aromatic region at δ 135.3–128.5 for dppe carbons, two complex groups of signals at about δ 29.6 and 25.0 due to two non-equivalent methylene carbons, and a signal at δ 23.13 attributable to the equivalent methyl carbons of the pyrimidine ligand. The ^{31}P NMR spectrum of [Cu_2(dmpymt)$_2$(dppe)$_3$] in $CDCl_3$ shows two signals at δ −9.19 and +31.2 that have shifted from δ −12.5 for dppe[24] in the same solvent, suggesting the presence of non-equivalent phosphorus donors; the signal at δ −9.19 is attributable to a bridging ligand and the one at δ +31.2 to two chelating dppe ligands.[22] Accordingly, we propose that the structure of this compound can be represented as [L(dppe)Cu(μ-dppe)Cu(dppe)L], S-monodentate pyrimidine-2-thionate completing tetrahedral $CuSP_3$ co-ordination around each copper atom. This is similar to the centrosymmetric structure of $[Cu_2L_2(dppe)_3]$ (L = benzothiazoline-2-thionate), in which there are two chelating dppe ligands and one bridging dppe ligand.[25]

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