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Design and synthesis of copper complexes of novel ligands based on the pyridine thiolate group †

Isamu Kinoshita,[a] L. James Wright,[b] Sachiko Kubo,[a] Kentaro Kimura,[a] Akio Sakata,[a] Toshihiro Yano,[a] Riichi Miyamoto,[a] Takanori Nishioka[a] and Kiyoshi Isobe[a]

[a] *Department of Materials Science, Graduate School of Science, Osaka City University, Osaka, 558-8585, Japan*

[b] *Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: isamu@sci.osaka-cu.ac.jp*

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The versatile coordination properties of 2,2′-dipyridyldisulfide (dpds) enables a series of different copper complexes to be isolated in good yield, including [$CuCl_2$(μ-dpds)] (**1**) which has a one-dimensional helical structure and [Cu(μ-Cl)(μ-dpds)] (**4**) which has a two-dimensional sheet structure. Flexible movement of the disulfide group in the dpds ligand facilitates the formation of complexes with a diverse range of structures. Compound **1** transforms into **4** almost quantitatively on standing in contact with methanol. After prolonged standing **4** slowly converts to the stable, betain-containing product, [Cu(μ-1-(2-pyridine)pyridiniumthiolato)(μ-Cl)] (**8**) with the concomitant production of elemental sulfur. The bromide congener of **4** undergoes the same transformation. The free ligand, 1-(2-pyridine)pyridiniumthiolate, can be released from **8** by treatment with CN^-. On treatment of bis(2-pyridylthio)methane (BPTM) with $CuCl_2$ [$CuCl_2$(BPTM)]$_n$ (**9**) is formed. This complex has an infinite helical chain structure. Reaction between tris(2-pyridylthio)methane (TPTMH) and CuBr gave [CuBr(TPTM)] (**12**) and with [Cu($NCCH_3$)$_4$]PF_6 in the presence of oxygen, the complex [Cu(CH_3CN)(TPTM)]PF_6 (**14**) is formed. Complex **14** is the first structurally characterised example of a complex containing a Cu(II)–C(sp^3) bond.

Introduction

The rich diversity of sulfur chemistry has long been recognized. This element plays an important role in inorganic chemistry, organic chemistry, and in many biological systems.[1] Pyridine-2-thiol (Hpyt) and pyridine-2-thiolate (pyt) are particularly versatile sulfur-containing ligands[2] and a number of studies have appeared that illustrate this point.[3–9] For example, copper(I) reacts with pyt to form the hexanuclear complex, [Cu(μ-pyt)]$_6$[10,11] and Hpyt can act as a bidentate ligand bridging between two metals to make either homo- or hetero-nuclear bimetallic complexes.[12–17] Umakoshi *et al.* have investigated the catalytic cleavage of sulfur from Hpyt using [Pt(5-mpyt)$_2$Pt] (5mpyt = 5-methylpyridine-2-thiolate).[18] Recently, Hpyt has been incorporated into ligands that are suitable for the assembly of metallosupramolecular materials and substituted crown ethers.[19,20] We have found that Hpyt and ligands incorporating this heterocyclic unit can undergo a number of unprecedented reactions that lead to novel structures and products,[21–23] some of which are of direct relevance to biological systems. For example, oxidation of bis(3-methyl-2-pyridine)disulfide with Cu(II) in the presence of air leads to the formation of a sulfonate derivative[22] in a process which mimics the metabolism of organic sulfur-containing molecules in mammals. We have also found examples where Cu(I/II) derivatives of Hpyt and related ligands undergo complex structural changes.

Experimental

All chemicals were purchased from Aldrich, Nacalai Tesque, and Wako Pure Chemicals. All reagents and solvents were used without further purification. IR spectra were recorded on a JASCO FT/IR-420 spectrophotometer in the range 4000–400 cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were measured on a JEOL Lambda 300, and a Lambda 400 spectrometer. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. CD spectra were recorded on a JASCO 720 CD spectrometer. FAB mass spectra were obtained with a JMS-700T spectrometer employing a 3-nitrobenzyl alcohol matrix. Electrochemical measurements were performed with a Bioanalytical System Inc. CV-50W voltammetric analyzer. Cyclic voltammograms were recorded at 25 °C by use of a glassy-carbon-disk working electrode and an Ag/AgCl reference electrode, dichloromethane or acetonitrile and 0.1 M Bu_4NPF_6 being used as solvent and supporting electrolyte, respectively. ESR spectra were recorded on a JEOL JES-TE300 spectrometer.

Elemental analyses were carried out by the Analytical Center of the Graduate School of Science in Osaka City University using a Perkin-Elmer 240C elemental analyzer.

Syntheses

[$CuCl_2$(μ-dpds)]$_n$ (1) (1D helical structure). Using an H-shaped cell (ϕ 1.7 cm and 12.5 cm lengths for the leg part, and ϕ 1.3 cm and 4.5 cm lengths for the bridging part), $CuCl_2$·$2H_2O$ (0.202 g, 1.18 mmol) and dpds (0.404 g, 1.83 mmol) were placed on the separate bottoms. Methanol (36 mL) was slowly added (over 2 min) and the solution left standing for one day at room temperature. From the bridging part of the H-shaped cell, dark-purple crystals of **1** were obtained (yield 40%). Anal. calc. for $C_{10}H_8N_2S_2CuCl_2$: C, 33.86; H, 2.27; N, 7.90. Found: C, 33.85; H, 2.22; N, 7.81%. IR (KBr; cm^{-1}): 1583 (s), 1556 (s), 1451 (s), 1416 (s), 1241 (m), 1151 (m), 1121 (m), 1082 (m), 1082 (m), 1050 (m), 1023 (m), 969 (w), 885 (w), 771 (s), 716 (w), 645 (w), 487 (w), 434 (w).

[(dpds)CuCl(μ-Cl)$_2$CuCl(dpds)] (2). $CuCl_2$·$2H_2O$ (0.033 g, 0.02 mmol) and dpds (0.032 g, 0.01 mmol) were added to 5 mL of dichloromethane in a small glass vessel (6 mL). The color of the solution turned to yellow–green. After the mixture was left for a month in the refrigerator (5 °C), green crystals of **5** were isolated (yield *ca.* 50%). Anal. calc. for $C_{10}H_8N_2S_2CuCl_2$: C, 33.86; H, 2.27; N, 7.90. Found: C, 33.72; H, 2.35; N, 7.83%.

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[$CuBr_2$(dpds)] (3). In a small vessel (6 mL), a dichloromethane solution (5 mL) of dpds (0.021 g, 0.95 mmol) was added to solid $CuBr_2$ (0.024 g, 0.10 mmol) at room temperature. The vessel was capped and left for one month. Red–brown crystals of **3** were obtained from the dark-brown solution (yield 10%). Anal. calc. for $C_{10}H_8N_2S_2CuBr_2$: C, 27.02; H, 1.82, N, 6.31. Found: C, 27.10; H, 1.88, N, 6.25%. IR (KBr; cm^{-1}): 1575 (s), 1552 (s), 1443 (s), 1416 (s), 1271 (w), 1226 (w), 1153 (w), 1118 (s), 1081 (m), 1049 (m), 996 (w), 776 (m), 753 (s), 714 (w), 484 (w), 434 (w).

[Cu(μ-Cl)(μ-dpds)]$_n$ (4) (2D net structure). Complex **4** was prepared from $Cu^{II}Cl_2$ (a) or $Cu^{I}Cl$ (b).

Method (a). The reaction of $Cu^{II}Cl_2{\cdot}2H_2O$ with dpds tended to form the one-dimensional helicate (**1**) as described above. Using an excess of dpds, the two-dimensional sheet structure (**4**) was obtained in reasonable yield. In an H-shaped cell (ϕ 1.7 cm and 12.5 cm lengths for the leg part, and ϕ 1.3 cm and 4.5 cm lengths for the bridging part), $CuCl_2{\cdot}2H_2O$ (0.080 g, 0.47 mmol) and dpds (0.472 g, 2.14 mmol) were allowed to react in 36 mL methanol at room temperature for one day. At first a small amount of the purple crystalline **1** was obtained. After prolonged standing of the solution for several days, the purple crystals disappeared, and yellow crystals of **4** were formed (yield *ca.* 60%).

Method (b). A colorless solution of dpds (0.720 g, 3.27 mmol) in CH_3CN (5 mL) was added dropwise to a yellow–green suspension of CuCl (0.042 g, 0.42 mmol) in CH_3CN (15 mL), forming a yellow solution. The vessel was sealed and left to stand at room temperature. After one hour small red crystals were produced on the surface of the remaining CuCl solid, but the red crystals disappeared within six hours. After standing for an additional 15 h, yellow crystals of **4** were isolated in *ca.* 50% yield. Anal. calc. for $C_{10}H_8N_2S_2CuCl$: C, 37.61; H, 2.53; N, 8.77. Found: C, 37.63; H, 2.44; N, 8.84%. IR (KBr; cm^{-1}): 1578 (s), 1556 (m), 1446 (s), 1416 (s), 1241 (w), 1155 (w), 1116 (w), 1085 (m), 1046 (m), 1021 (m), 775 (s), 753 (s), 710 (m), 645 (w), 489 (m).

[Cu(μ-Br)(dpds)]$_2$ (5) (dinuclear). To an H-shaped tube, (ϕ 1.7 cm and 12.5 cm lengths for the leg part, and ϕ 1.3 cm and 4.5 cm lengths for the bridging part), a methanol solution (5 mL) of $CuBr_2$ (0.025 g, 0.11 mmol) and a methanol solution (5 mL) of dpds (0.22 g, 1.0 mmol) were carefully added to the separate bottoms. After addition of methanol (29 mL) to immerse the bridging part, this solution was left to stand for 1 week in the refrigerator (5 °C). From the bridging part of the H-tube, red crystals appeared (yield 27%). Further standing of the solution tends to make the red crystals disappear and leads to growth of the yellow crystals. The yield of **5** was not good due to the thermal instability of the product crystals. Special care was required to reproduce the experiment and the following factors should be kept precisely: the dimensions of the H-shaped cell, concentration, temperature, and the period of time the solution is left standing to obtain the crystals. Anal. calc. for $C_{10}H_8N_2S_2CuBr$: C, 33.02; H, 2.22; N, 7.70. Found: C, 32.95; H, 2.15; N, 7.62%.

[Cu(μ-Br)(μ-dpds)]$_n$ (6) (2D net structure). Complex **6** was prepared from $Cu^{II}Br_2$ (a) or $Cu^{I}Br$ (b).

Method (a). In a 50 mL vessel, a methanol solution (20 mL) of dpds (0.166 g, 0.75 mmol) was added during 2 min to a methanol (15 mL) solution of $CuBr_2$ (0.134 g, 0.60 mmol) at room temperature. The vessel containing the resulting yellow solution was capped and left at room temperature. Yellow crystals of **6** were obtained from the solution after 13 days (yield 90%).

Method (b). A suspension of $Cu^{I}Br$ (0.068 g, 0.47 mmol) in 15 mL of acetonitrile was stirred efficiently, resulting in a pale-blue solution with a small residue. A colorless solution of dpds (0.485 g, 2.20 mmol) in 5 mL of acetonitrile was added slowly into the solution with an immediate observation of yellow and red spots on the solid surface of the remaining $Cu^{I}Br$. After 1 day, the red spots disappeared and a small amount of yellow crystals formed. After one month of standing the yield of crystalline **6** was 89%. Anal. calc. for $C_{10}H_8N_2S_2CuBr$: C, 33.02; H, 2.22; N, 7.70. Found: C, 32.90; H, 2.10; N, 7.68%. IR (KBr; cm^{-1}): 1575 (s), 1552 (s), 1443 (s), 1416 (s), 1273 (w), 1226 (w), 1152 (w), 1118 (s), 1083 (m), 1049 (m), 996 (w), 774 (m), 753 (s), 714 (w), 625 (w), 483 (w), 437 (w).

[Cu(μ-Cl)(μ-ppt)]$_n$ (7). This complex was formed by a ligand rearrangement reaction with C–S bond cleavage and N–C bond formation. The yield was low because of the formation of side products. From the mixture of $CuCl_2{\cdot}2H_2O$ (0.037 g, 0.22 mmol) and dpds (0.218 g, 1.0 mmol) in 12 mL of methanol, purple crystals of **1** were obtained (yield 7%). After removal of these crystals, the green–yellow filtrate was allowed to stand for a month, during which time yellow crystals of **4** formed (yield 49%). After removing these by filtration, the yellow filtrate was left to stand for several months. The desired orange crystals of **7** were then obtained (yield 12%). Anal. calc. for $C_{10}H_8N_2SCuCl$: C, 41.81; H, 2.81; N, 9.75. Found: C, 41.76; H, 2.77; N, 9.72%. IR (KBr; cm^{-1}): 1587 (s), 1511 (m), 1452 (m), 1372 (m), 1263 (m), 11226 (s), 855 (w), 749 (s) 477 (w), 418 (w).

[Cu(μ-Br)(μ-ppt)]$_n$ (8). This complex was prepared by three different methods.

Method (a). $CuBr_2$ (0.124 g, 0.56 mmol) and dpds (0.909 g, 4.13 mmol) were placed in a glass vessel (55 mL), and 35 mL of methanol was added. When the mixture was allowed to stand at room temperature, yellow crystals of **5** formed within two weeks. After further standing of the crystals in solution for several months, the yellow crystals gradually disappeared, and orange crystals of **8** were obtained in *ca.* 70% yield. A large crystal of elemental sulfur (S_8) was obtained at the same time (*ca.* 30% in crystalline form and *ca.* 40 % from solution).

Method (b). A small amount of complex **8** was obtained from a reaction of $Cu^{I}Br$ (0.010 g, 0.07 mmol) and dpds (0.027 g, 0.13 mmol) in 15 mL of methanol. The desired product, **8**, was obtained as orange crystals among yellow crystals of **5** (yield *ca.* 10%).

Method (c). On refluxing an equimolar amount of $Cu^{II}Br_2$, dpds and $Ce(NH_3)_2(NO_3)_4$ in methanol for one day, **8** was obtained quantitatively as an orange microcrystalline powder. Anal. calc. for $C_{10}H_8N_7SCuBr$: C, 36.21; H, 2.43; N, 8.45. Found: C, 36.46; H, 2.37; N, 8.47%. IR (KBr; cm^{-1}): 1582 (s), 1509 (s), 1448 (m), 1407 (w), 1370 (m), 1261 (m), 1123 (s), 888 (w), 848 (w), 749 (s), 718 (w), 477 (m).

Isolation of 1-(2-pyridyl)pyridinium-2-thiolate (ppt) and the production of bis(2-pyridylthio)methane (BPTM). The orange complex, [CuBr(ppt)]$_n$ (5.67 g, 17.1 mmol) was added to a 200 mL aqueous solution of KCN (11.7 g, 179 mmol) and stirred for 10 minutes. The yellow solution obtained was extracted with four 50 mL portions of CH_2Cl_2. The CH_2Cl_2 extracts were combined and evaporated, then purified by silica-gel column chromatography, eluting with CH_2Cl_2–CH_3CN (8 : 1). The first fraction was recrystallized with toluene. 1-(2-Pyridyl)pyridinium-2-thiolate was obtained as white crystals (1.38 g, 7.33 mmol yield 43%). Anal. calc. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88. Found: C, 63.34; H, 4.11; N, 14.69%. ^{1}H NMR ($CDCl_3$): δ 8.63 (d, $^3J_{H-H}$ = 3.09 Hz, 1H), 7.91~7.85 (m, 1H), 7.74~7.69 (m, 3H), 7.44~7.39 (m, 1H). IR (KBr; cm^{-1}): 1622 (s), 1590 (s), 1572 (m), 1526 (s), 1466 (s), 1456 (s), 1436 (s), 1408 (s), 1298 (m), 1275 (w), 1220 (w), 1179 (w), 1148 (s), 1089 (s), 1053 (m), 1028 (w), 1012 (s), 992 (m), 849 (w), 787 (m), 774 (s), 749 (s), 718 (s), 634 (w), 616 (m), 563 (s), 515 (w), 485 (m), 459 (m), 415 (m).

From the aqueous solution, white crystals appeared. The structure was shown by X-ray crystallography to be bis(pyridyl-2-thio)methane but the yield was only 3%. This material was prepared in much higher yield by the following method: to a 200 mL aqueous solution containing KOH (4.80 g, 84.9 mmol), pyridine-2-thiol (3.76 g, 33.8 mmol) and CH_2Cl_2 (1.4 g, 16.9 mmol) was added and heated under reflux for 12 h under argon. The solution was extracted four times with 100 mL of CH_2Cl_2. The CH_2Cl_2 extracts were combined, evaporated, then purified by silica-gel column chromatography, with CH_2Cl_2–CH_3CN (8 : 1) as eluant. The first fraction was recrystallized with toluene. White crystals of bis(pyridyl-2-thio)methane were obtained (yield 45%). Anal. calc. for $C_{11}H_{10}N_2S_2$: C, 56.38; H, 4.30; N, 11.95. Found: C, 56.23; H, 4.25; N, 11.83%. ^{1}H NMR ($CDCl_3$): δ 8.46 (d, $^3J_{H–H}$ = 4.80 Hz, 2H, 6-py), 7.47~7.45 (m, 2H, 4-py), 7.16 (d, $^3J_{H–H}$ = 8.04 Hz, 2H, 3-py), 7.00~6.98 (m, 2H, 5-py), 5.06 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 157.72 (2-py), 149.44 (6-py), 136.02 (4-py), 122.50 (3-py), 119.71 (5-py), 30.83 (CH_2). IR (KBr; cm^{-1}): 1606 (w), 1578 (s), 1554 (s), 1467 (m), 1455 (s), 1413 (s), 1337 (m), 1286 (m), 1244 (w), 1214 (m), 1173 (w), 1145 (m), 1123 (s), 1087 (m), 1041 (m), 986 (m), 963 (w), 876 (w), 867 (w), 794 (m), 756 (s), 714 (s), 665 (w), 620 (w), 477(m), 445 (w).

Tris(2-pyridylthio)methane (TPTM). This complex was prepared by a different method to that recently reported.[24] To a 200 mL aqueous solution containing KOH (4.80 g, 84.9 mmol), pyridine-2-thiol (3.76 g, 33.8 mmol) and $CHBr_3$ (2.85 g, 11.3 mmol) was added and sonicated for 60 min at 50 °C. The solution was extracted four times with 100 mL of CH_2Cl_2. The CH_2Cl_2 extracts were combined, evaporated, then purified by silica-gel column chromatography, using CH_2Cl_2–CH_3CN (8 : 1) as eluant. The first fraction was recrystallized with toluene. White crystals of bis(pyridyl-2-thio)methane were obtained in 60% yield. Anal. calc. for $C_{16}H_{13}N_3S_3$: C, 55.95; H, 3.81; N, 12.23. Found: C, 55.90; H, 3.70; N, 12.00%. ^{1}H NMR ($CDCl_3$): δ 8.50 (d, $^3J_{H–H}$ = 4.88 Hz, 3H, 6-py), 7.88 (s, 1H, CH), 7.52~7.48 (m, 3H, 4-py), 7.23 (d, $^3J_{H–H}$ = 8.03 Hz, 3H, 3-py), 7.04~7.00 (m, 3H, 5-py), ^{13}C NMR ($CDCl_3$): δ 157.53 (2-py), 149.61 (6-py), 136.31 (4-py), 122.20 (3-py), 120.23 (5-py), 49.19 (CH). IR (KBr; cm^{-1}): 1575 (s), 1557 (s), 1454 (s), 1412 (s), 1279 (m), 1245 (w), 1194 (w), 1177 (w), 1146 (m), 1126 (s), 1109 (m), 1085 (m), 1044 (m), 984 (m), 960 (w), 876 (w), 756 (s), 720 (s), 710 (m), 617 (w), 483 (m), 453 (w).

Preparation and optical resolution of 6-methyl-1-[2-(3-methyl)-pyridyl]pyridinium-2-thiolate (6,3-mppt). This complex was prepared by two different methods.

Method (a). A solution of KOH (0.37 g, 6.6 mmol) in methanol was added dropwise to a methanol solution containing 1*H*-6-methylpyridine-2-thione (0.82 g, 6.6 mmol). The mixture was then stirred at room temperature for 20 min. The solvent was removed under reduced pressure. The residue was dissolved in 30 mL of 1,2-propanediol, and then 2-bromo-3-methylpyridine (1.1 g, 6.6 mmol) was added to the mixture. After heating under reflux for 1 day, the reaction mixture was evaporated to dryness under reduced pressure. The black residue was dissolved in 50 mL of water, and then extracted with four, 40 mL portions of toluene. The toluene solution was dried for 1 day over 10 g of magnesium sulfate anhydride. The toluene was evaporated, and the resulting residue was purified by silica-gel column chromatography using CH_2Cl_2–CH_3CN (8 : 1) as eluant. The R_f value of 6,3-mppt was *ca.* 0.5. The material obtained from the appropriate fraction removed from the column was recrystallized from diethyl ether to afford pure 6,3-mppt (0.018 g, yield 1.2%) as a yellow solid. 6,3-mppt was characterized by FAB-MS and NMR spectroscopy. Anal. calc. for $C_{12}H_{12}N_2S{\cdot}0.1H_2O$: C, 66.08; H, 5.64; N, 12.85. Found: C, 66.00; H, 5.53; N, 12.70%. FAB-MS: *m*/*z* 217 [M + H]$^+$.

Method (b). A degassed suspension of 2,2′-bis(3-methylpyridyl)disulfide (3-mpds) (0.17 g, 0.67 mmol) and 2,2′-bis-(6-methylpyridyl)disulfide (6-mpds) (0.17 g, 0.67 mmol) in methanol (50 mL) was added to a degassed solution of $CuBr_2$ (0.45 g, 2.0 mmol) in methanol (50 mL). The mixture was heated at reflux for 1 day under an argon atmosphere. The resulting yellowish orange precipitate was removed by filtration and dried. The yellowish orange solid was then added to 30 mL of water, and the mixture was stirred for 10 min to afford an orange suspension. To this suspension was added potassium cyanide (0.80 g, 12 mmol) in small portions with stirring. The resulting clear solution was extracted with five 50 mL portions of toluene. The extracts were combined and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2–CH_3CN (8 : 1) as eluant. The first yellow band with an R_f value of 0.5 was collected, and the solvent was evaporated. The resulting 6,3-mppt was recrystallized from diethyl ether (0.049 g, yield 17%). Anal. calc. for $C_{12}H_{12}N_2S{\cdot}0.1H_2O$: C, 66.08; H, 5.64; N, 12.85. Found: C, 66.08; H, 5.48; N, 12.78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (s, CH_3), 2.49 (s, CH_3), 6.68 (dd, CH, J = 6.6, 6.6 Hz), 7.37 (dd, CH, J = 4.7, 7.6 Hz), 7.42 (d, CH, J = 6.6 Hz), 7.51 (d, CH, J = 6.6 Hz), 7.72 (d, CH, J = 7.6 Hz), 8.47 (d, CH, J = 4.7 Hz). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 17.29 (s, CH_3), 23.05 (s, CH_3), 111.96 (s, CH), 124.80 (s, CH), 130.34 (s), 133.73 (s, CH), 137.10 (s, CH), 140.20 (s, CH), 143.22 (s), 147.42 (s, CH), 155.95 (s), 180.78 (s). UV-Vis (2-propanol): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 283 (11400), 369 (6860). FAB-MS: *m*/*z* 217 [M + H]$^+$. IR (KBr): 1616 (s), 1575 (m), 1546 (s), 1454 (s), 1420 (s), 1375 (s), 1286 (m), 1269 (m), 1229 (w), 1169 (m), 1139 (s), 1092 (m), 1072 (s), 1001 (m), 884 (w), 809 (m), 775 (m), 762 (m), 747 (m), 718 (m), 656 (m), 591 (m).

The ^{1}H- and ^{13}C-NMR spectra of the compound obtained by this method were identical to that of the compound prepared by the direct coupling method.

Optical resolution of the compounds was performed by a HPLC system equipped with a chiral stationary phase (CHIRALCEL OD, Daicel Chemical Ind., Ltd.). The eluting solvent, 2-propanol, was passed into the column (30 °C) at a constant flow rate of 0.2 mL min^{-1}. The enantiomers were effectively separated with retention times of 21 and 23 min. Each band containing the enantiomers was collected separately, and then the circular dichroism spectra were measured. The CD profile of the first eluted isomer was a mirror image of the profile for the second. The intensity of the CD signal for the optically resolved 6,3-mppt was decreased by almost one half after standing in solution at room temperature for four days.

[Cu(Cl)$_2$(μ-BPTM)]$_n$ (9). $CuCl_2{\cdot}2H_2O$ (0.040 g, 0.23 mmol) and BPTM (0.01 g, 0.04 mmol) were allowed to react in 10 mL methanol at room temperature for two days in an H-shaped cell (ϕ 1.0 cm and 3.5 cm lengths for the leg part, and ϕ 1.0 cm and 2.0 cm lengths for the bridging part). After this time dark green crystals of **9** were obtained (6 mg, 0.016 mmol, 38% based on BPTM). Anal. calc. for $C_{11}H_{10}Cl_2CuN_2S_2$: C, 35.82; H, 2.73; N, 7.60. Found: C, 35.61; H, 2.71; N, 7.50%. IR (KBr; cm^{-1}): 1591 (s), 1560 (s), 1464 (s), 1420 (s), 1293 (s), 1235 (m), 1206 (w), 1168 (s), 1139 (s), 1102 (m), 1059 (m), 1016 (m), 1011 (m), 977 (w), 965 (w), 772 (s), 759 (s), 744 (m), 731 (m), 644 (m), 494 (w), 487 (w), 431 (m).

[Cu(Br)$_2$(μ-BPTM)]$_n$ (10). To a solution of CuBr (12 mg, 0.084 mmol) in 2 mL acetonitrile, a solution of BPTM (20 mg, 0.85 mmol) in 2 mL acetonitrile was added and left to stand for 3 weeks. Green crystals of **10** were obtained, (yield 4 mg, 10%). Anal. calc. for $C_{11}H_{10}Br_2CuN_2S_2$: C, 28.86; H, 2.20; N, 6.12. Found: C, 28.59; H, 2.19; N, 6.02%. IR (KBr; cm^{-1}): 1589 (s), 1558 (s), 1464 (s), 1423 (s), 1409 (s), 1285 (s), 1235 (w), 1204 (m), 1168 (m), 1154 (s), 1135 (m), 1092 (m), 1055 (m), 1028 (m), 1015 (m), 971 (w), 964 (w), 900 (m), 874 (w), 852 (m), 778 (m),

762 (s), 737 (m), 726 (m), 649 (w), 640 (w), 619 (w), 495 (m), 434 (m), 423 (w).

[Cu_2I_4(BPTM)$_2$] (11). CuI (0.016 g, 0.085 mmol) and BPTM (0.02 g, 0.0485 mmol) were allowed to react in 10 mL methanol at room temperature for three weeks in an H-shaped cell (ϕ 1.0 cm and 3.5 cm lengths for the leg part, and ϕ 1.0 cm and 2.0 cm lengths for the bridging part). Yellow crystals of **11** were obtained, yield 13 mg, 50%. Anal. calc. for $C_{22}H_{20}Cu_4I_4N_4S_4$: C, 21.47; H, 1.64; N, 4.55. Found: C, 21.62; H, 1.46; N, 4.37%. IR (KBr; cm^{-1}): 1644 (w), 1583 (s), 1560 (s), 1477 (w), 1456 (s), 1422 (s), 1375 (s), 1288 (m), 1281 (s), 1229 (w), 1203 (s), 1165 (s), 1140 (m), 1122 (s), 1092 (m), 1057 (s), 1051 (s), 1006 (s), 959 (w), 884 (m), 869 (w), 825 (s), 762 (s), 751 (s), 733 (m), 726 (s), 709 (m), 648 (w), 634 (m), 489 (s), 430 (w), 413 (s).

Reaction of TPTMH with Cu(I) salts

The reaction of TPTMH with Cu(I) salts produces several different complexes depending upon the conditions used.

[CuBr(TPTM)] (12) and [Cu_4Br_4(dpds)$_2$]$_n$ (13). An acetonitrile solution (10 mL) of CuBr (42 mg, 0.29 mmol) was mixed with TPTMH (100 mg, 0.29 mmol) in 10 mL acetonitrile. The solution was stirred for 12 h. The yellow precipitate that formed was removed by filtration and the filtrate left to stand for 2 weeks. During this time deep purple crystals of **12** were obtained (62 mg, 44%). Anal. calc. for $C_{16}H_{12}BrCuN_3S_3$: C, 39.55; H, 2.49; N, 8.65. Found: C, 39.48; H, 2.35; N, 8.37%. IR (KBr; cm^{-1}): 1587 (s), 1556 (s), 1453 (s), 1421 (s), 1281 (s), 1237 (w), 1195 (w), 1158 (m), 1135 (s), 1092 (m), 1047 (s), 1004 (s), 974 (w), 885 (w), 766 (s), 724 (s), 667 (w), 635 (m), 490 (m), 466 (w), 411 (m). If the yellow precipitate was not removed from the mother liquor, yellow crystals of the tetranuclear complex **13** were obtained (13 mg, 18%). Anal. calc. for $C_{20}H_{16}Br_4Cu_4N_4S_4$·$2CH_2Cl_2$: C, 22.31; H, 1.70; N, 4.73. Found, $C_{20}H_{16}Br_4Cu_4N_4S_4$·$3CH_2Cl_2$: C, 21.77; H, 1.31; N, 4.21%. IR (KBr; cm^{-1}): 1604 (m), 1587 (s), 1516 (m), 1442 (m), 1369 (m), 1349 (w), 1272 (m), 1234 (w), 1157 (w), 1125 (s), 1105 (w), 1083 (w), 1036 (w), 1005 (w), 983 (w), 920 (w), 903 (w), 866 (w), 755 (s), 720 (m), 714 (w), 623 (w), 486 (m), 438 (w), 430 (w).

[Cu(CH_3CN)(TPTM)]PF_6 (14). An acetonitrile (10 mL) solution of [Cu(CH_3CN)$_4$]PF_6 (113 mg, 0.303 mmol) was mixed with TPTMH (100 mg, 0.29 mmol) in air. The color of the solution gradually turned to purple, then purple crystals contaminated with a small amount of orange crystals were obtained. The mixture of crystals were isolated by filtration and separated by hand. The yield of purple crystalline **14** was 104 mg (60%). Anal. calc. for $C_{18}H_{15}CuF_6N_4PS_3$: C, 36.52; H, 2.55; N, 9.46. Found: C, 36.58, H, 2.55; N, 9.52%. IR (KBr; cm^{-1}): 2285(m), 1587 (s), 1559 (m), 1456 (s), 1424 (m), 1284 (m), 1159 (m), 1135 (m), 1048 (w), 1008 (w), 881 (s), 839 (s), 766 (s), 723 (m), 557 (s).

X-Ray crystallography

For **1**–**4** and **7**–**9** data were collected on a Rigaku AFC-7R diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.5418 Å) for **1** and a Rigaku AFC-7S diffractometer using Mo-Kα radiation (λ = 0.7107 Å) for the others. AFC/MSC software was used for collection, processing, and correction for Lorentzian and polarization effects. Empirical absorption corrections were applied to the intensity data by use of ψ scans. No significant alterations were observed in the control intensities monitored every 150 reflections except for **7**. A linear decay correction was applied for **7**.

For **14** data were collected on a Rigaku AFC-7/Mercury CCD area-detector diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). CrystalClear software was used for the collection, processing, and correction for Lorentzian and polarization effects. An absorption correction was applied based on comparison of multiple symmetry equivalent measurements.

The structures were solved by a combination of Sir92[25] direct method and Fourier difference syntheses and refined by full matrix least-squares against F^2 using SHELXS-97[26] and teXsan[27] as a graphical interface. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were found on difference Fourier maps and refined isotropically.

A summary of the crystal data, data collection and refinement is given in Table 1.

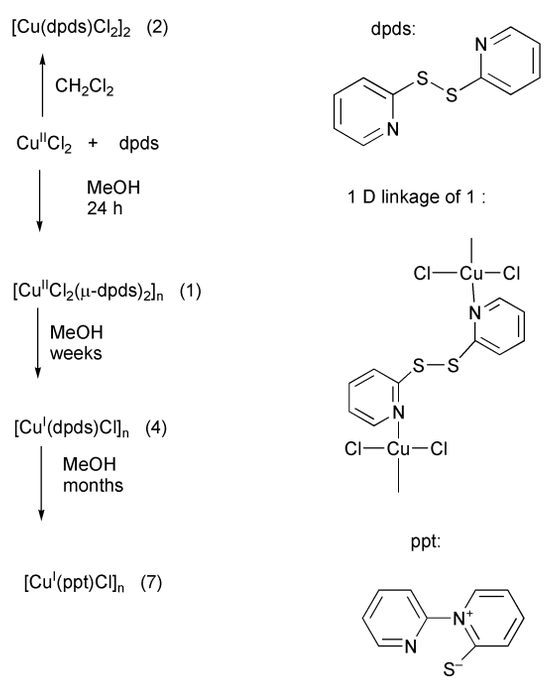
CCDC reference numbers 195987–195994.

See http://www.rsc.org/suppdata/dt/b2/b210420m/ for crystallographic data in CIF or other electronic format.

Results and discussion

Preparation and characterization of the complexes

Treatment of $CuCl_2$ with 2,2′-dipyridyldisulfide (dpds) at ambient temperature leads to the formation of a series of isolable, quasi-stable complexes as indicated in Scheme 1. Depending on the conditions, either [$CuCl_2$(μ-dpds)$_2$]$_n$ (**1**) or [$CuCl_2$(dpds)]$_2$ (**2**) can be isolated in reasonable yields. Purple, hexagonal shaped crystals of **1** were obtained in *ca.* 40% yield after one day by the slow, diffusion-controlled reaction of $CuCl_2$ with dpds in methanol using an H-shaped reaction vessel. The structure of **1**, which was determined by X-ray crystallography, reveals that this material is comprised of one-dimensional, extended polymeric chains of "[$CuCl_2$(dpds)]" units in which the dpds ligands bridge between the copper atoms (see Fig. 5, later). The polymer chains have a helical structure. The space group of the crystal studied was either $P3_1$ or $P3_2$ and thus the crystal necessarily only contained one optical isomer. In this case the polymeric chain had P-helicity. The pyridine rings in one helicate form π–π stacking interactions with the pyridine rings in three neighboring helicates. The shortest inter-ring π–π stacking distance is 3.4 Å.



Scheme 1

If the $CuCl_2$ and dpds were left to react for longer than one day in the H-shaped reaction vessel, the amount of the purple crystalline material, **1**, that formed did not increase any further. Instead, yellow crystals began to appear. These have been identified as the Cu(I)-containing material, [Cu^I(μ-Cl)(μ-dpds)]$_n$ (**4**).

Table 1 Crystallographic data for **1**–**4**, **8**, **9** and ppt

Compound	**1**	**2**	**3**	**4**	**8**	ppt[c]	**9**	**14**
T/K	296.2	296.2	296.2	296.2	296.2	296.2	296.2	296.2
Formula	$CuC_{10}H_8Cl_2N_2S_2$	$Cu_2C_{20}H_{16}Cl_4N_4S_4$	$CuC_{10}H_8Br_2N_2S_2$	$CuC_{10}H_8ClN_2S_2$	$CuC_{10}H_8BrN_2S$	$C_{10}H_8N_2S$	$CuC_{11}H_{10}Cl_2N_2S_2$	$CuC_{18}H_{15}F_6N_4PS_3$
M	354.76	709.52	443.66	319.31	331.70	188.25	368.79	592.03
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P3_1$ (no. 144)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)
a/Å	8.3704(9)	7.530(1)	13.241(2)	7.933(3)	7.655(1)	6.655(1)	12.476(1)	14.414(2)
b/Å	8.3704(9)	8.2269(9)	7.499(1)	15.061(2)	8.821(1)	6.641(2)	8.4932(9)	10.132(2)
c/Å	16.774(2)	11.618(1)	14.093(1)	10.383(2)	9.4081(9)	10.4614(7)	13.1982(8)	15.605(2)
α/°	90	87.87(1)	90	90	72.237(9)	90	90	90
β/°	90	73.02(1)	102.203(9)	112.43(2)	72.262(9)	90.288(8)	99.004(6)	91.534(4)
γ/°	120	71.86(1)	90	90	67.494(10)	90	90	90
U/Å^3	1017.8(2)	653.0(2)	1367.7(3)	1146.6(4)	546.0(1)	456.3(1)	1381.3(2)	2278.4(6)
Z	3	1	4	4	2	2	4	4
μ(Mo-Kα)/mm^{-1}	8.586[b]	2.376	7.740	2.470	5.825	0.303	2.250	1.368
F(000)	531.00	354.00	852.00	640.00	324.00	196.00	740.00	1188.00
Data collected	2352	4059	2233	3686	3374	3104	4461	22495
Unique data (R_{int})	2016 (0.018)	3812 (0.007)	2004 (0.018)	3338 (0.018)	3184 (0.007)	2663 (0.016)	4027 (0.032)	5117 (0.040)
Observed data [$I > 2\sigma(I)$]	2003	3310	1555	2440	2587	2433	2588	3700
Final R_1 [$I > 2\sigma(I)$][a]	0.0306	0.0244	0.0290	0.0312	0.0303	0.0286	0.0396	0.0415
wR_2	0.0857	0.0631	0.0700	0.0687	0.0737	0.0828	0.0978	0.1054

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] μ(Cu-Kα)/mm^{-1}. [c] ppt = 1-(2-pyridyl)pyridinium-2-thiolate.

After prolonged standing (*ca.* 1–2 weeks) the amount of **1** diminished significantly and the yield of **4** increased to 60–80%. Single crystal X-ray structure determination of **4** showed that this material contains a two-dimensional extended sheet structure.

The reaction between $CuCl_2$ and dpds gives a different product if the solvent used is CH_2Cl_2. After standing in the H-shaped reaction vessel for one week, green crystals of the dimeric complex, $[CuCl_2(dpds)]_2$ (**2**) were deposited. This complex did not change to the yellow Cu(I) complex, **4**, on standing. Although the yields of **1** and **4** are relatively high, these complexes are only quasi-stable, and further reactions proceed to give **7** by prolonged standing of the solution.

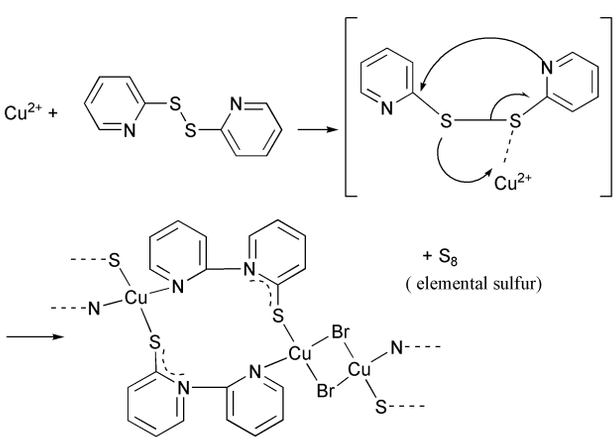
The reaction of dpds with $CuBr_2$ in methanol does not give a product with a helical structure as in **1** nor does it give a dimeric Cu(II) product with a structure corresponding to that of **2**. Instead, a complex with the formula $[Cu(\mu\text{-}Br)(dpds)]_2$ (**5**)[21] is formed, and this has a similar molecular structure to that of the chloride congener, $[Cu(\mu\text{-}Cl)(dpds)]_2$, although its sensitivity toward light or heat is much greater. The red crystals of **5** are rather difficult to isolate because when left in contact with the MeOH solvent that is used for the synthesis of this compound, spontaneous rearrangement to $[Cu(\mu\text{-}Br)(\mu\text{-dpds})]_n$ **6** (see Scheme 2) occurs.

Scheme 2

Single crystal X-ray crystallography has revealed that **6** has a two-dimensional sheet structure analogous to that observed for the chloride analog, **4**. Crystals of the meta-stable dimer **5** can be stored unchanged for extended periods at room temperature if light is rigorously excluded. Upon irradiation of solid samples of **5** with UV light, the crystals change color from red to yellow as conversion to **6** occurs. The appearance of a small yellow spot on a single crystal initiates rapid transformation of the whole crystal to the new structure. The close similarity in the extended arrangement of atoms found in the crystal structures of $[Cu(\mu\text{-}Br)(dpds)]_2$, and $[Cu(\mu\text{-}Br)(\mu\text{-}dpds)]_n$ (see below) undoubtedly facilitates this solid state transformation. One possible mechanism by which this rearrangement could occur involves initial cleavage of the S–S bonds in the dpds ligands followed by rotation of the pyridine rings about the Cu–N bonds and then reformation of the bridging S–S bonds between adjacent pyridine units to regenerate the dpds ligands in a position bridging between two copper centers (see Scheme 2).[21]

The chloride congener, $[Cu(\mu\text{-}Cl)(dpds)]_2$, was much less prone to undergo this structural transformation. The greater differences in the extended arrangements of atoms in the crystal structures of the chloride congeners of **5** and **6** compared with those found in the bromide analogs are probably a significant factor in determining this reduced reactivity.

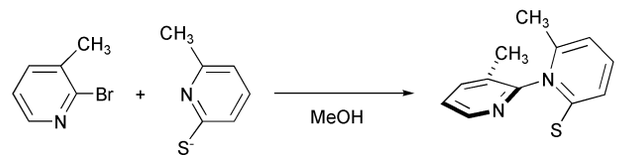
The compounds $[Cu(\mu\text{-}Cl)(\mu\text{-}dpds)]_n$ (**4**) and $[Cu(\mu\text{-}Br)(\mu\text{-}dpds)]_n$ (**6**) can both be prepared directly by treatment of the corresponding Cu(I) halides with dpds in methanol at room temperature for a day. The yields of these two-dimensional sheet materials reached 50 and 90% for the chloride and bromide derivatives respectively. If these same reagents are allowed to react together for more than a month at room temperature, or they are heated under reflux in methanol for one day, further reaction occurs and the corresponding betain-containing materials, $[Cu(ppt)Cl]_n$ (**7**) or $[Cu(ppt)Br]_n$ (**8**) are formed (see Schemes 1 and 2). During this process the dpds ligands are converted into the coordinated betain, 1-(2-pyridyl)pyridinium-2-thiolate (ppt), with accompanying extrusion of elemental sulfur. The process is inhibited in the absence of oxygen which suggests that oxidation of Cu(I) to Cu(II) is necessary for the reaction to proceed. Indeed, in the presence of $Ce(NH_3)_2(NO_3)_4$ the reaction produces **8** almost quantitatively. The yield of elemental sulfur is almost the same as the yield of the final betain-containing complexes in all these reactions. A possible mechanism for this betain-forming reaction is presented in Scheme 3.



Scheme 3

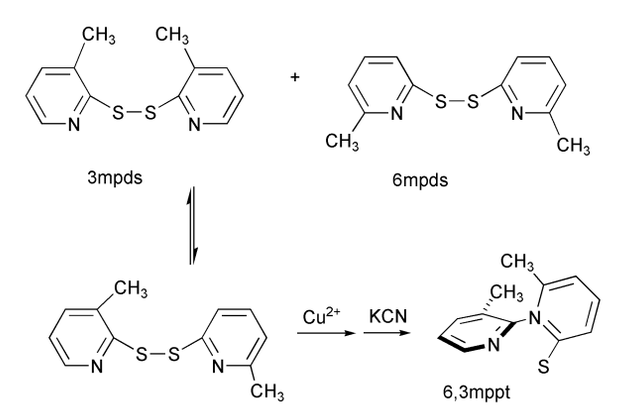
Single crystal X-ray structure determination of **8** shows that the 1-(2-pyridyl)pyridinium-2-thiolate (ppt) ligands do not coordinate through the S and N donor atoms to one copper ion even though in doing so they would form six-membered chelate rings. Instead, they act as bridging ligands between two copper(I) atoms. Presumably the rigidity of the ppt ligand makes chelate ring formation unfavorable in this case. The copper(I) atoms are also bridged by the halide ions thereby building up the one-dimensional polymeric chains found in the structure. Free 1-(2-pyridyl)pyridinium-2-thiol can be formed by treatment of $[Cu(\mu\text{-}Cl)(\mu\text{-}ppt)]_n$ with potassium cyanide.

Following this reaction, we have designed a potentially optical active ppt by the reaction of 2,2′-bis(6-methylpyridine)-disulfide (6-mpds) and 2,2′-bis(3-methylpyridine)disulfide (3-mpds) with Cu(II). Initially we tried to make the target betain, 6-methyl-1-[2-(3-methyl)pyridyl]pyridinium-2-thiolate, by direct synthesis as shown in Scheme 4. The yield of this reaction was less than 2%.



Scheme 4

The total yield of the betain was much improved by using the following procedure (Scheme 5). A mixture of 2,2′-bis(3-methylpyridyl)disulfide (3-mpds) and 2,2′-bis(6-methylpyridyl)-disulfide (6-mpds) in methanol was added to a degassed solution of $CuBr_2$ in methanol, and then the mixture was heated under reflux for 1 day under an argon atmosphere. The resulting yellowish orange precipitate was treated with potassium cyanide, extracted with toluene. This product contained several isomers since the 3-mpds and 6-mpds equilibrate with the mixed 3,6-mpds before reaction with Cu(II) occurs,. Silica-gel column chromatography gave pure 6,3-mppt in 17% yield. Of the three possible mppt products (3,3-mppt, 6,6-mppt and 6,3-mppt), only 6-methyl-1-[2-(3-methyl)pyridyl]pyridinium-2-thiolate (6,3-mppt) is chiral. In order to separate the two enantiomers of 6,3-mppt, the yellow–orange, betain-containing product was subjected to HPLC chromatography using a chiral stationary phase (CHIRALCEL OD, Daicel Chemical Ind., Ltd.). The two enantiomers of 6,3-mppt were effectively separated with retention times of 21 and 23 min using 2-propanol as eluant. As shown in Fig. 1, the CD profile of the first eluted isomer is a mirror image of the profile for the second. This result clearly indicates that the two bands separated by the HPLC method correspond to the 6,3-mppt enantiomers which arise from the axial chirality around the C–N bond in the molecules. The optically resolved 6,3-mppt racemizes with $t_{1/2}$ = *ca*. 4 days.



Scheme 5 Ligand abbreviations: 3-mpds = 2,2′-bis(3-methylpyridyl)-disulfide; 6-mpds = 2,2′-bis(6-methylpyridyl)disulfide (6-mpds); 6,3-mppt = 6-methyl-1-[2-(3-methyl)pyridyl]pyridinium-2-thiolate.

During attempts to isolate 1-(2-pyridyl)pyridinium-2-thiolate, bis(pyridylthio)methane was formed as a side product through reaction between dichloromethane and pyridine-2-thiol. The yield of this material was increased if the reaction

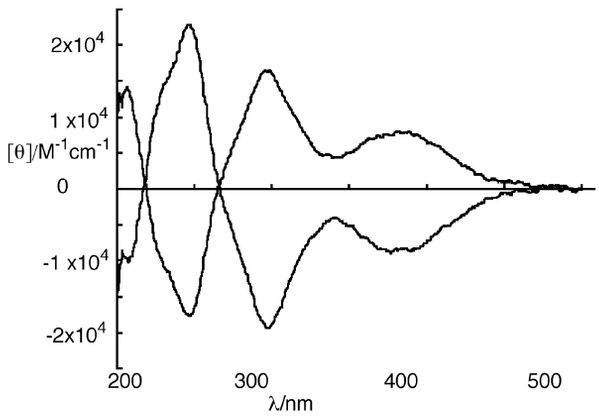
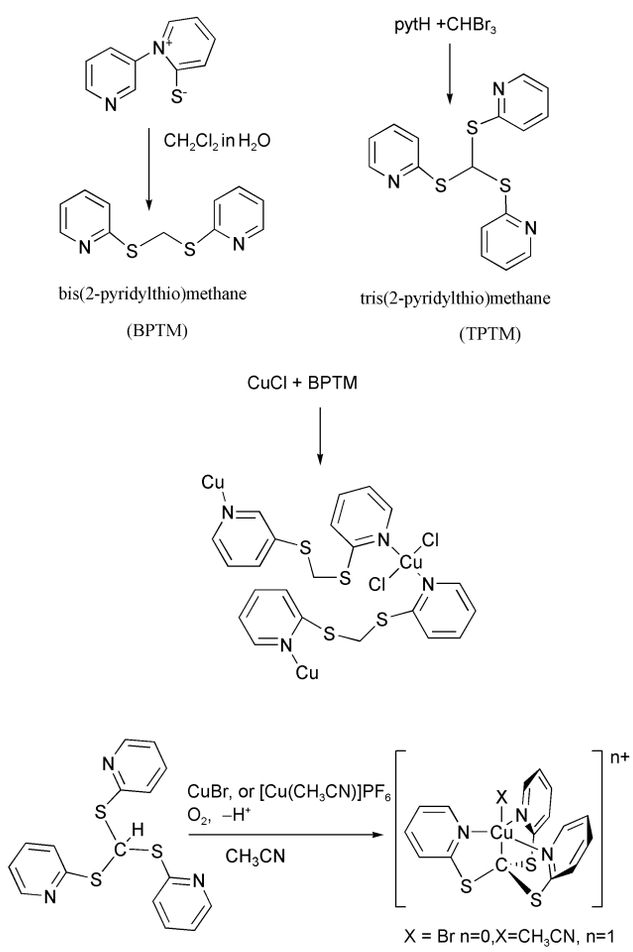


Fig. 1 CD spectra of resolved 6,3-mppt in 2-propanol.

between dichloromethane and pyridine-2-thiol was carried out in water. In an extension of this chemistry, the new ligand Tris(2-pyridylthio)methane (TPTMH) was designed and synthesised through reaction between tribromomethane and pyridine-2-thiol. Very recently another group has reported the synthesis of this ligand.[24]

A very interesting product, $[Cu(TPTM)(CH_3CN)]PF_6$ (**14**), is formed when $[Cu(CH_3CN)_4]PF_6$ is treated with TPTMH in the presence of oxygen (Scheme 6). The Cu(II) atom in **14** forms bonds to the three pyridine nitrogen atoms, the acetonitrile nitrogen and surprisingly, the central, bridging sp^3-hybridised carbon atom of the ligand. Exclusion of oxygen during the reaction prevented the formation of this Cu–C bond, suggesting that removal of the hydrogen atom and formation of the Cu–C bond occurred during the oxidation process. Previously we have found that oxidation of sulfur in dpds by oxygen occurs



Scheme 6

Table 2 Electrochemical data for $[Cu(TPTM)(CH_3CN)]PF_6$ and [CuBr(TPTM)]

	E/V ($E_{pa} - E_{pc}$)
[Cu(TPTM)(CH_3CN)]	
CH_2Cl_2	**−0.174 (0.089), 0.65 (0.100)**
CH_3CN	−0.327 (0.064), 0.654 (pc)[a]
[CuBr(TPTM)]	
CH_2Cl_2	−0.691 (pa),[a] 0.462 (0.063)
CH_3CN	−0.359 (0.065), 0.512 (0.084)

$TBAPF_6$ 0.1 M, (Fc/Fc^+ = 0.4 V), glassy carbon electrode.[a] Irreversible, the peak positions are cited.

in the presence of Cu(I).[22] The formation of **14** proceeds without the addition of base, and a closely related complex, [CuBr(TPTM)] (**12**), is formed under the same conditions if the copper substrate used is CuBr. Well characterized organometallic compounds containing Cu(II)–C bonds are extremely rare. The only other reported examples are found in N-confused porphyrins.[28,29] Complex **14** appears to be the first fully characterised compound containing a Cu(II)–C(sp^3) bond.

Electrochemical and spectroscopic properties of [CuBr(TPTM)] (12), and $[Cu(TPTM)(CH_3CN)]PF_6$ (14)

The complexes **12** and **14** are stable as solids and in CH_3CN or CH_2Cl_2 solutions. In acetonitrile, $[Cu(TPTM)(CH_3CN)]PF_6$ (**14**) displays interesting electrochemistry (Table 2, Fig. 2). It has a reversible Cu(I)/Cu(II) couple and an irreversible oxidation wave for the Cu(II)/Cu(III) process. In contrast, [CuBr(TPTM)] (**12**) in acetonitrile has a reversible Cu(I)/Cu(II) reduction wave which is very close to the value observed for **14**, as well as a quasi-reversible Cu(II)/Cu(III) oxidation wave. In addition to the quasi-reversible wave, **12** has an irreversible peak at 0.65 mV. In CH_2Cl_2 both processes become reversible for $[Cu(TPTM)(CH_3CN)]PF_6$ (**14**), suggesting that all three oxidation states, $[Cu(TPTM)(CH_3CN)]^{0/+/2+}$, are accessible. In contrast to this result, [CuBr(TPTM)] has only a reversible oxidation wave whereas the reduction wave becomes irreversible. These processes suggest the following possibilities. The reduced form of

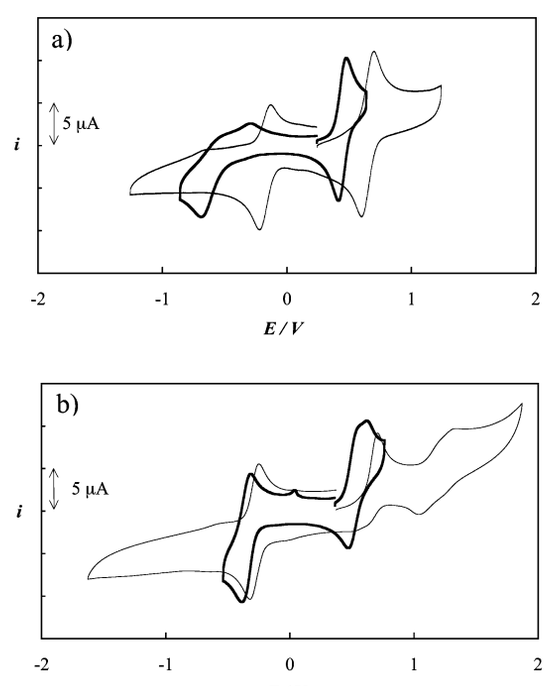


Fig. 2 Cyclic voltammetry of $[Cu(CH_3CN)(TPTM)]PF_6$ (thin line) and [CuBr(TPTM)] (thick line) in (a) CH_2Cl_2 and (b) CH_3CN.

14 is stable, and **12** is in equilibrium with **14** in CH_3CN. In CH_2Cl_2, the oxidation wave for both **14** and **12** become reversible, indicating the presence of five coordinate Cu(III) complexes of the form, $[CuX(TPTM)]^{0/+}$. The irreversible nature of the reduction wave for **12** indicates that the five-coordinate Cu(I) state is unstable for this compound.

Absorption spectra of both $[Cu(TPTM)(CH_3CN)]PF_6$ (**14**) (416 nm, $\varepsilon = 2400$ dm^3 mol^{-1} cm^{-1}, 557 nm, $\varepsilon = 1260$ dm^3 mol^{-1} cm^{-1}) and [CuBr(TPTM)] (396 nm, $\varepsilon = 1080$ dm^3 mol^{-1} cm^{-1}, 543 nm $\varepsilon = 880$ dm^3 mol^{-1} cm^{-1}) have similar absorption peaks that can be assigned as LMCT bands involving the anionic TPTM ligand and the copper ion. The CV results for **14** in CH_2Cl_2 indicate that in principle it should be possible to detect the Cu(III) state. Accordingly, complex **14** was oxidized in CH_2Cl_2 at +1 V (*vs.* NHE) and the absorption spectrum was measured *in situ* (Fig. 3). Three new peaks appeared (340 nm, $\varepsilon = 1710$ dm^3 mol^{-1} cm^{-1}, 445 nm, $\varepsilon = 2000$ dm^3 mol^{-1} cm^{-1}, and 554 nm, $\varepsilon = 7240$ dm^3 mol^{-1} cm^{-1}). The original spectrum of **14** was reproduced after re-reduction of the sample at 0.0 V. This measurement suggests that a stable Cu(III) complex with essentially the same structure as **14** is formed, and this could tentatively be formulated as $[Cu(CH_3CN)(TPTM)]^{2+}$.

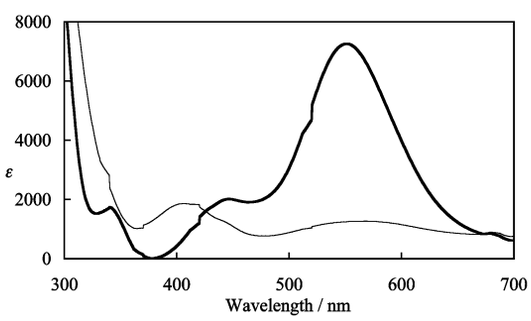


Fig. 3 Absorption spectra of **14** in an electrolysis cell: (a) in CH_2Cl_2 before electrolysis (b) after electrolysis and measured *in situ*.

The ESR spectrum of $[Cu(TPTM)(CH_3CN)]^+$ (Fig. 4) in frozen glass ($[Cu(TPTM)(CH_3CN)]PF_6$ in $CH_3CN : CH_2Cl_2 : C_3H_7CN = 1 : 1 : 1$) shows $g_{xx,yy} = 2.0$ ($A = 55$ G) $g_{zz} = 2.13$ ($A = 100$ G) indicating a d_{z^2} ground state.[29–34] This value indicates a trigonal bipyramidal structure for the complex in solution. A similar solution structure was determined for the copper(II) complexes, [CuX(tmpa)] (X = Cl, Br; tmpa = tris(pyridylmethyl)amine), which show the same ESR patterns. In contrast, [CuX(pmap)] (pmap = bis[2-(2-pyridyl)ethyl](2-pyridyl)methylamine), which contains longer chains on two of the pyridine groups, has a square pyramidal structure in both the solid state and in solution.[35,36] The presence of the sulfur atoms attached to the bridging carbon atom in the TPTM ligand does not cause the structure of the copper complex **14** to deviate from the trigonal bipyramidal arrangements that are observed for [CuX(tmpa)], and this geometry is retained even in a solvent like acetonitrile.

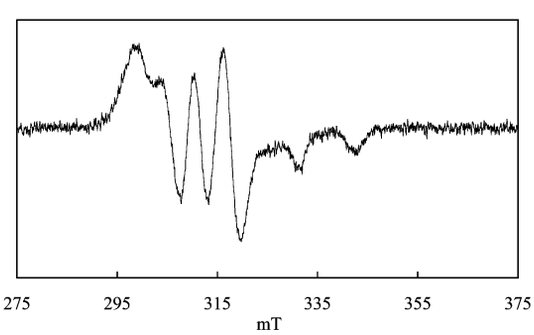


Fig. 4 Frozen glass ESR spectrum of $[Cu(CH_3CN)(TPTM)]PF_6$ in $CH_3CN : CH_2Cl_2 : C_3H_7CN = 1 : 1 : 1$.

Single crystal X-ray structure determinations of new copper complexes of ligands incorporating the pyridine-2-thiolate unit

The syntheses of a variety of copper complexes of ligands that incorporate the pyridine-2-thiolate unit have been described. Many of the isolated complexes are meta-stable and some undergo further rearrangements in the solid state. The key technique that has allowed the characterisation of many of these materials is single crystal X-ray crystallography. In the following section, details of the X-ray structure determinations of the new complexes are discussed.

$[CuCl_2(\mu\text{-dpds})_2]_n$ (1). The structure of this complex is interesting because of its novel helical arrangement. The spontaneous construction of a helical system requires a reasonable origin for the helicity. In this case the supramolecular, helical structure of the copper(II) compound with 2,2′-dipyridyldisulfide (2-dpds) resembles that found in helical peptides. 2-dpds has two pyridine units that can coordinate to metals, and one disulfide bond that is susceptible to reductive or photochemical cleavage. These two properties make this ligand a fruitful unit for the synthesis of multi-metallic systems.

Purple crystals of $[CuCl_2(\mu\text{-dpds})_2]_n$ (**1**) crystallize in the chiral space group $P3_1$ or $P3_2$. One of the most important features of the crystal structure of **1** is the presence of the 3_1 axis along with the infinite, polymeric chains, $[CuCl_2(\mu\text{-dpds})_2]_n$ (see Fig. 5). Each Cu(II) atom is in a plane defined by two Cl^- and two mutually *trans* pyridine N atoms. All the 2-dpds ligands bridge Cu(II) atoms thus constructing infinite chains. Because of the presence of the 3_1 axis, all the $[CuCl_2(\mu\text{-dpds})_2]_n$ units are related to each other by symmetry. This particular crystal has been refined as $P3_1$. Under this space group, the

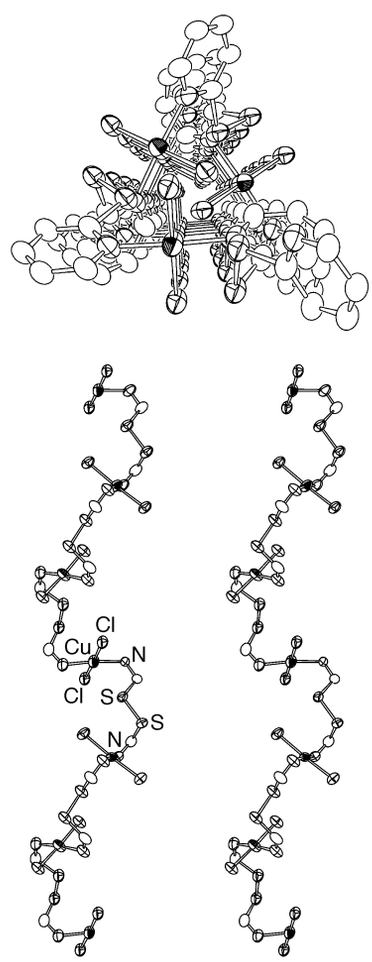


Fig. 5 ORTEP[37] drawing of **1** with a view along the 3_1 axis in the $P3_1$ space group (upper) and a stereoscopic view of the helicate. Part of the pyridine rings are removed for clarity.

$[CuCl_2(\mu\text{-dpds})_2]_n$ units are arranged with P helicity. In this crystal, the shortest distance between Cu(II) atoms is 6.414(9) Å for intra-chain metals and the shortest distance for inter-chain metals is 7.673(1) Å. The structure of the helical chain is determined by the conformation of 2-dpds. The parameters that determine the conformation of 2-dpds are rotation around the S–S, and two C–S bonds. In this crystal, the C–S–S–C torsion angle is set at 98.4(7)° so as to satisfy the 3_1 axis along the *c*-axis. The S–S–C–N torsion angle of 100.2(3)° enables links to be made to the Cu atoms while the square planar coordination geometry about the copper centers is maintained. The helical structure in this crystal is strongly supported by the π–π interactions between helical chains. All pyridine rings have very short inter-ring C · · · C distances of 3.4 Å.

$[CuCl_2(\mu\text{-dpds})_2]_2$ (2). The reaction of dpds with $CuCl_2$ produces several Cu(II) complex other than the helical complex **1**. Such diversity mainly comes from the flexibility and freedom of rotation around the S–S bond. As one of the main products, we have cited complex **2** which was prepared in dichloromethane. This complex can be viewed as having a dinuclear structure as shown in Fig. 6. However, when viewed this way the structure has two very long Cu–Cl bonds, longer than the sum of ionic radii of the Cu(II) and Cl^- (2.54 Å) as well as unusually long Cu–S bonds. In this case each Cu ion is surrounded by a tridentate dpds ligand and one terminal Cl. In addition, two bridging chlorides complete the approximately octahedral coordination geometry about each Cu center. The bonds between Cu(1) and the two chloride ligands Cl(1) and Cl(2) are short (Cu(1)–Cl(1) = 2.3369(5) and Cu(1)–Cl(2) = 2.2366(5) Å) while the bond to Cl(1)* is very long (Cu(1)–Cl(1)* = 2.7177(5) Å).

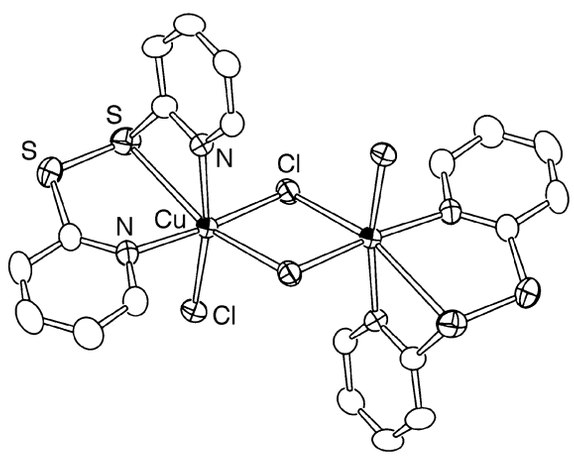


Fig. 6 ORTEP drawing of **2**, shown as a dimer.

The sulfur atom of the disulfide group is coordinated to Cu(1) at a distance of 2.8466(6) Å, which is also very long and much longer than the average Cu–S bond length (2.67 Å).[14] Because of the length of the Cu–S and Cu–Cl(1)* distances, the existence of significant bonding interactions between these atoms is debatable. The structure of **2** is that it consists of monomeric, four coordinate, square planar copper units. The square planar Cu(II) center is coordinated by two chloride ions and the two pyridyl nitrogen atoms of the dpds ligand. Neither of the sulfur atoms coordinate to the Cu atom, and the dpds ligand forms a seven-membered chelate ring.

$[CuBr_2(dpds)]$ (3). The coordination geometry about the Cu(II) ion in **3** is approximately tetrahedral with bonds being formed to two bromide ions and the two pyridyl nitrogen atoms of a single dpds ligand. These latter interactions result in the formation of a seven-membered chelate ring (see Fig. 7). Each molecule of $[CuBr_2(dpds)]$ has a crystallographic mirror plane. The lengths of the Cu–N and Cu–Br bonds are 1.972(2) and 2.3696(4) Å respectively. The coordination angles for Br(1)–Cu–N(1), Br(1)–Cu–N(1)*, Br(1)–Cu–Br(1)* and N(1)–Cu–N(1)*, are 97.57(7), 96.45(7), 137.59(3) and 140.6(1)° respectively. Interestingly, $[Cu^{II}Br_2(dpds)]$ shows only this type of distorted tetrahedral structure.

Table 3 S–S Bond distances (Å) and C–S–S–C torsion angles (°) for Cu(II) complexes **1**–**3**

	1	**2**	**3**
	S–S		
	2.031(2)	2.024(1) 2.047(1)	2.059(2)
	C–S–S–C		
	71.1(2)	71.1(2) 81.3(2)	108.9(2)

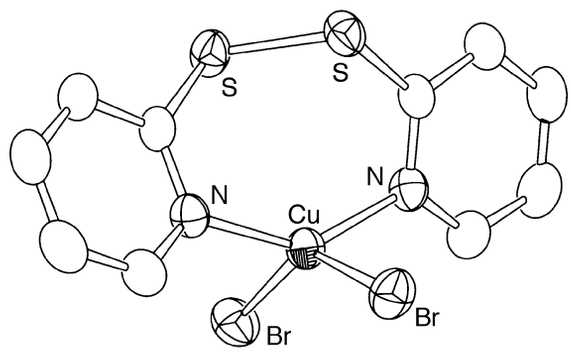


Fig. 7 ORTEP drawing of $[CuBr_2(dpds)]$ (**3**).

The characteristics of the dpds complexes of Cu(II) can be summarised as follows: (1) With $CuCl_2$, a range of complexes can be isolated. One main product has a one-dimensional helical structure. Other discrete complexes with Cu(II) ions form square planar arrangements. (2) With $CuBr_2$ only one product, complex **3**, is obtained. It has a distorted tetrahedral structure with a Br–Cu–Br angle of 137.59(3)°. (3) The S–S bond distances range from 2.026(1) to 2.059(2) Å with the two sulfur atoms not involved in coordination to the Cu(II) center. (4) The C–S–S–C torsion angles of the products derived from $CuCl_2$ are smaller than the corresponding torsion angle of the product **3** which is derived from $CuBr_2$ (see Table 3). The smaller torsion angles of **1** and **2** resemble those of the free 2-dpds ligands (86.5(1) and 87.1(1)°). The large torsion angle of complex **3** may cause some instability in this compound, and this might possibly trigger the observed conversion into the two-dimensional net structure.

Crystal structures of dpds and ppt complexes of Cu(I)

In a previous report, we investigated the light-induced polymerization of the dimeric complex, $[Cu(\mu\text{-Br})(dpds)]_2$, (**5**) to $[Cu(\mu\text{-Br})(\mu\text{-dpds})]_n$ (**6**).[21] These compounds have the same empirical formula, [CuBr(dpds)], and similar atomic arrangements to each other. The results obtained suggested that light-induced polymerization was taking place. Similar structures have been found for the corresponding chloride derivatives. Aerobic ethanol solutions containing **1**,**4**,**5**, or **6** produced both [Cu(μ-X)(μ-ppt)] (**7**, X = Cl; **8**, X = Br) and elemental sulfur, S_8 on standing for long periods or when heated under reflux. The structures of **7** and **8** are quite similar to each other, and so only the structure of **8** is discussed below.

$[Cu(\mu\text{-Br})\{1\text{-(2-pyridyl)pyridinium-2-thiolate}\}]_n$ (8). [Cu(μ-X)-(μ-ppt)] (**8**) has a one-dimensional infinite chain structure (see Fig. 8). The ligand, 1-(2-pyridyl)pyridinium-2-thiolate (ppt, Fig. 9), was formed by the reaction of dpds as shown in Scheme 3. Copper ions are alternatively connected in chains by bridging bromides or ppt. Each copper ion is surrounded in a tetrahedral

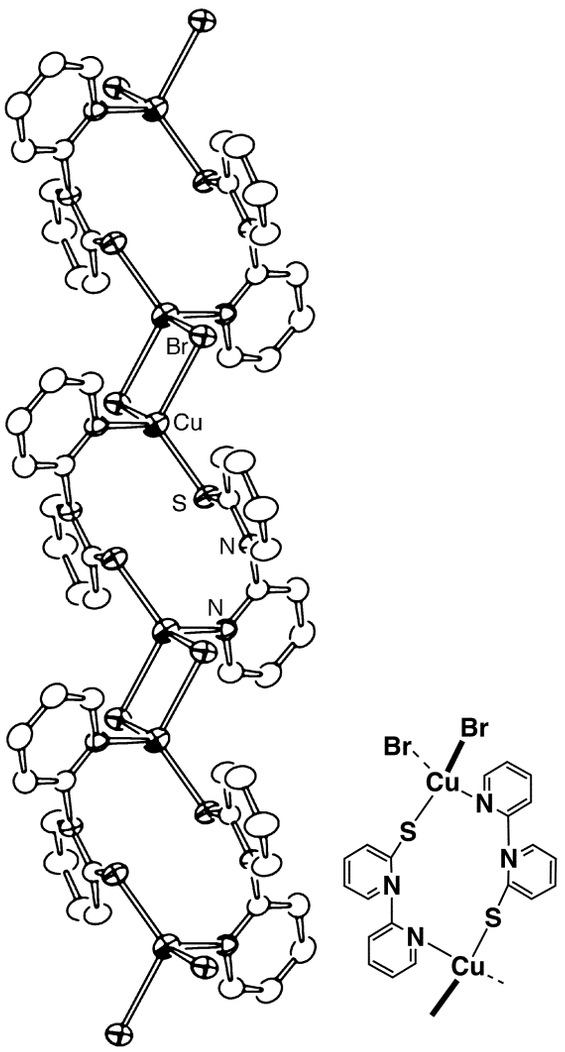


Fig. 8 ORTEP drawing of **8** along with a schematic representation.

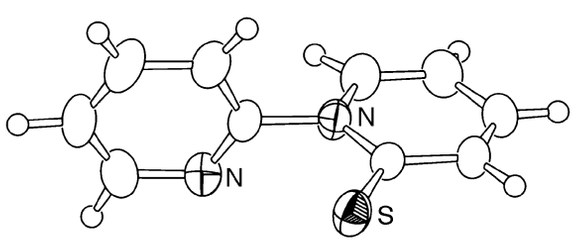


Fig. 9 ORTEP drawing of ppt.

arrangement by two bromides, one sulfur atom from a thiolate group, and one nitrogen atom from a pyridyl group. An inversion center is located at the middle of each Cu · · · Cu vector within a chain. The bond lengths around each Cu(II) are 2.4633(5) (Cu–Br), 2.5902(5) (Cu–Br), 2.2622(8) (Cu–S) and 2.131(2) Å (Cu–N). The pyridinium ring is essentially planar with the bond angles around the pyridinium nitrogen atom within the range 116.7(2)–122.9(2)° indicating that the aromatic nature of this ring is retained. The structure of the isolated ppt ligand was also determined. Comparison of the structural parameters with those obtained for the coordinated ligand revealed that the bond angles and bond lengths are almost identical, except for the torsion angle between two pyridine rings.

The crystal structure of BPTM related complexes

During the course of isolating the ligand ppt, we obtained the compound bis(2-pyridylthio)methane (BPTM). Using this compound, we have prepared some copper complexes and these turned out to have several different types of coordination. One of these products, $[CuCl_2(BPTM)]_n$ (**9**), can be obtained in good yield from the reaction of BPTM with $CuCl_2$. The structure of **9** consists of infinite helical chains (see Fig. 10). Two chloride ions coordinate to each Cu(II) atom in mutually *trans* positions, and each BPTM ligand bridges between two adjacent copper atoms to form the helical chains. In this way each copper atom forms bonds to two pyridine nitrogen atoms from two different BPTM ligands. The Cu–N bond lengths are 2.047(3) and 2.045 Å, and Cu–Cl distances are 2.2840(9) and 2.261(1) Å.

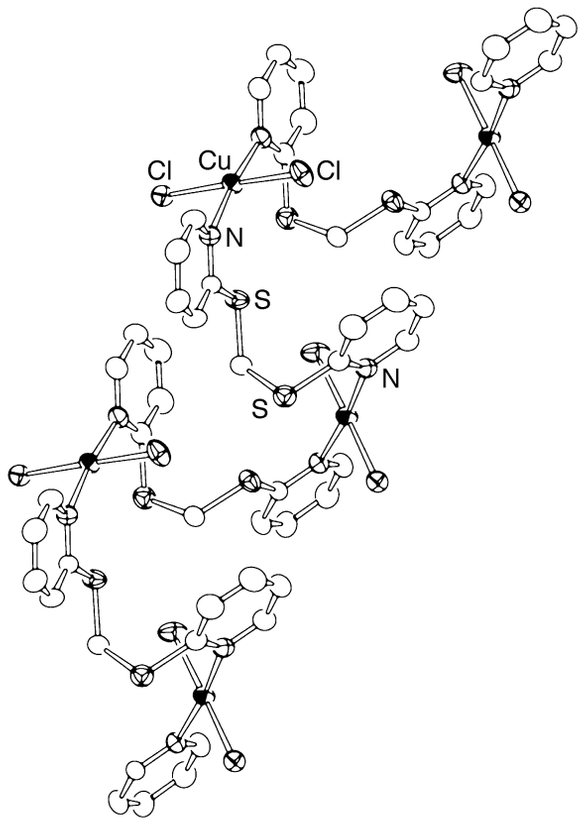


Fig. 10 ORTEP drawing of **9**.

$[Cu(TPTM)(CH_3CN)]PF_6$ (14). The single crystal X-ray structure determination of **14** has been completed and the molecular geometry is depicted in Fig. 11. The ligands are arranged about the copper atom in this mononuclear complex

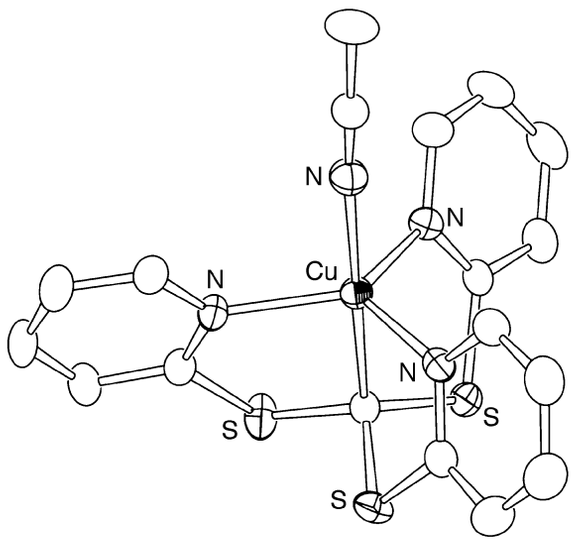


Fig. 11 ORTEP drawing of **14**.

in a trigonal bipyramidal fashion. The copper atom is coordinated by the three pyridine nitrogen atoms of the TPTM ligand, the nitrogen atom of the acetonitrile and, surprisingly, the deprotonated, bridging sp^3 hybridised carbon atom of the TPTM ligand. This is the first observation of a compound containing a Cu(II)–C(sp^3) bond. The Cu–C bond length is 2.004(3) Å. The Cu–N(acetonitrile) bond length is 2.028(3) Å. The three Cu–N(py) bonds are 2.077(3), 2.084(3) and 2.074(3) Å. The structure indicates the presence of strong axial coordination causing a d_{z^2} ground state.

Conclusions

It has been shown that ligands incorporating the pyridine-2-thiolate group display widely varied and interesting coordination chemistry with Cu(I) and Cu(II). With 2,2′-dipyridyldisulfide (dpds), it is possible to isolate a series of complexes with diverse structural elements that include monomers, dimers, one-dimensional helical chains and two-dimensional sheets. The reactivity of the S–S and the C–S bonds of the disulfide in these complexes facilitates several very interesting transformations. One of these involves the conversion of a simple dimeric structure into a two-dimensional sheet structure through a mechanism that appears to involve scission and reformation of the disulfide S–S bonds. In another example elemental sulfur is extruded during the rearrangement of dpds to the betain 1-(2-pyridyl)pyridinium-2-thiol. The newly synthesised ligands bis(2-pyridylthio)methane (BPTM) and tris(2-pyridylthio)-methane (TPTMH) also coordinate to copper. In the presence of oxygen, $[Cu(NCMe)_4]^+$ reacts with TMTPH forming the novel Cu(II) complex $[Cu(TPTM)(CH_3CN)]PF_6$ which contains the first example of a compound containing a Cu(II)–C(sp^3) bond. During the oxidation of the Cu(I) center by oxygen, the bridging carbon atom of the ligand is deprotonated and the Cu(II)–C bond formed.

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