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Synthesis and characterisation of cobalt(III), nickel(II), copper(I) and silver(I) complexes of silylated pyridine-2-thione

José A. García-Vázquez,*[a] Jaime Romero,*[a] Antonio Sousa-Pedrares,[a] María L. Louro,[a] Antonio Sousa*[a] and Jon Zubieta[b]

[a] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706-Santiago de Compostela, Spain*
[b] *Department of Chemistry, Syracuse University, Syracuse, NY 13244, USA*

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The electrochemical oxidation of anodic metal (cobalt, nickel, copper and silver) in acetonitrile solutions of the appropriate heterocyclic thione, $RMe_2SipySH$ (3-$Bu^tMe_2SipySH$, 3-$ThexMe_2SipySH$, 6-$ThexMe_2SipySH$) gave complexes of general formula $[M(RMe_2SipyS)]$ (M = Cu, Ag) and $[M(RMe_2SipyS)_n]$ (when M = Co, $n = 3$; M = Ni, $n = 2$). When the oxidation was repeated in the presence of 2,2′-bipyridine (bipy), the mixed complexes $[M(RMe_2SipyS)_2(bipy)]$ were obtained only in the case of M = Ni. The reaction between copper complexes, $[M(RMe_2SipyS)]$, and 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm) in acetonitrile yielded $[Cu_2(RMe_2SipyS)_2(dppe)_3]$ and $[Cu_2(RMe_2SipyS)_2(dppm)_2]$. The molecular structures of $[Cu_6(3\text{-}Bu^tMe_2SipyS)_6]$, **1**, $[Cu_6(6\text{-}ThexMe_2SipyS)_6]$, **2**, and $[3\text{-}Bu^tMe_2SipyS\text{-}Spy\text{-}3\text{-}Bu^tSiMe_2]$, **3**, were determined by X-ray diffraction. Compounds **1** and **2** are hexanuclear with the six copper atoms arranged in a distorted octahedral geometry and each copper atom in a distorted trigonal planar $[CuS_2N]$ environment, each ligand adopting the N,S-bidentate S-bridging mode. The electronic, vibrational and ^1H and ^{13}C NMR spectra of the complexes are discussed and related to the structure.

Metallic complexes of heterocyclic thiones have been widely studied because of their relevance to biological systems and the versatility in their coordination forms (neutral monodentate,[1,2] bridging[3] through S, anionic S-monodentate,[4] chelating[5] or bridging between two[6] or three[7] metals atoms yielding numerous complexes with unusual geometries, variable nuclearities and great structural diversity.[8]

As part of our continuing interest in the heterocyclic thione complexes of low nuclearities,[9] this paper reports the electrochemical syntheses of complexes of cobalt, nickel, copper and silver with 3(*tert*-butyldimethylsilyl)pyridine-2-thione (3-$Bu^tMe_2SipySH$), 3-thexyldimethylsilylpyridine-2-thione (3-$ThexMe_2SipySH$) and 6-thexyldimethylsilylpyridine-2-thione (6-$ThexMe_2SipySH$). These bulky ligands were used in the hope that steric influences would modify the aggregation process. The aggregation process can also be modified by blocking some coordination sites with additional ligands, such as 2,2′-bipyridine, 1,2-bis(diphenylphosphine)ethane (dppe) or bis(diphenylphosphine)methane (dppm).

Experimental

General considerations

Cobalt, nickel, copper and silver (Ega Chemie) were used as plates (*ca.* 2 × 2 cm). Pyridine-2-thione, diisopropylamine, chloro-*tert*-butyldimethylsilane, chlorodimethylthexylsilane, bis(diphenylphosphine)methane and 1,2-bis(diphenylphosphine)ethane were commercial products (Aldrich) and were used without further purification. n-Butyllithium (2 M in hexane) and tetrabutylammonium fluoride (1.0 M in tetrahydrofuran) were purchased from Aldrich as solutions. Microanalysis of all compounds was done using a CHNS Carlo Erba 1108 elemental analyser. IR spectra were recorded in KBr mulls on a Bruker IFs 66v spectrophotometer and ^1H and ^{13}C NMR spectra recorded on a Bruker WM 350 MHz using $CDCl_3$ or DMSO-d_6 as solvents. Chemical shifts were determined against TMS.

Preparation of the ligands

All manipulations were carried out under argon, using conventional Schlenk techniques. Solvents used to isolate the products were distilled over appropriate drying agents, degassed and saturated with argon, by passing argon through them for 1 h. The silylated ligands were prepared following a modified literature method.[10]

Synthesis of 3-(thexyldimethylsilyl)pyridine-2-thione (3-Thex-$Me_2SipySH$), 6-(thexyldimethylsilyl)pyridine-2-thione (6-Thex-$Me_2SipySH$) and 3,6-(thexyldimethylsilyl)pyridine-2-thione (3,6-$ThexMe_2SipySH$). Dry diisopropylamine (25 ml, 18 g, 178 mmol) was added dropwise to a stirred solution of n-butyllithium (178 mmol; 71.3 ml of a 2.5 M solution in hexane) at −78 °C under an argon atmosphere. After addition of 200 ml of dry THF, the cooling bath was removed, and the mixture was stirred at room temperature. It was again cooled to −78 °C and a solution of pyridine-2-thione (6 g, 54 mmol) in 100 ml of THF was added slowly with stirring and the reaction was allowed to reach room temperature.

The solution was again cooled to −78 °C and chlorodimethylthexylsilane (29 g, 32 ml, 162 mmol) was slowly added. The final solution was allowed to stand with stirring at room temperature for 45 hours. After this time, water (100 ml) was slowly added, the organic phase separated and then evaporated to dryness. The resultant yellow oil was dissolved in ether (250 ml), and water (300 ml) was added. The aqueous phase was extracted with ether (3 × 50 ml) and the organic phase dried with anhydrous Na_2SO_4. Ether was evaporated, and the crude material dissolved in a small amount of hexane, and subjected to flash chromatography on silica gel (hexane–ethyl acetate). This resulted in the isolation of 3-(thexyldimethylsilyl)pyridine-

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2-thione (1.6 g, 11.7%), 6-(thexyldimethylsilyl)pyridine-2-thione (1.83 g, 13.4%) and 3,6-bis(thexyldimethylsilyl)pyridine-2-thione (4.4 g, 20.6%).

3-(Thexyldimethylsilyl)pyridine-2-thione. Anal. Calc. for $C_{13}H_{23}NSSi$: C, 61.60; H, 9.15; N, 5.53; S, 12.65. Found: C, 61.98; H, 9.10; N, 5.23; S, 12.20%. IR (KBr, cm^{-1}): 3180 (m), 3050 (w), 2950 (s), 1580 (s), 1550 (s), 1480 (s), 1405 (w), 1350 (w), 1285 (s), 1260 (m), 1160 (vs), 1104 (m), 820 (vs), 670 (m), 570 (m), 450 (m). ^{1}H NMR ($CDCl_3$): δ 13.1 (s, NH), 7.6 (d, H^4), 6.7 (d, H^5), 7.5 (d, H^6), 0.4 (s, H^a), 1.0 (s, H^b), 0.8 (d, H^c), 1.7 (m, H^d). ^{13}C NMR ($CDCl_3$): δ 181 (C^2), 146 (C^6), 136 (C^4), 144 (C^3), 113 (C^5), 34 (C^e), 35 (C^d), 22 (C^c), 19 (C^b), −2 (C^a).

6-(Thexyldimethylsilyl)pyridine-2-thione. Anal. Calc. for $C_{13}H_{23}NSSi$: C, 61.60; H, 9.15; N, 5.53; S, 12.65. Found: C, 61.29; H, 9.21; N, 5.62; S, 12.42%. IR (KBr, cm^{-1}): 3136 (m), 3070 (w), 3024 (m), 2925 (s), 1545 (s), 1512 (m), 1467 (m), 1390 (m), 1359 (m), 1302 (s), 1250 (m), 1163 (w), 1039 (w), 1004 (w), 835 (s), 819 (vs), 804 (vs), 759 (s), 729 (w). ^{1}H NMR ($CDCl_3$): δ 13.0 (s, NH), 7.4 (d, H^3), 7.2 (d, H^4), 6.7 (d, H^5), 0.35 (s, H$^{a'}$), 0.8 (s, H$^{b'}$), 0.9 (d, H$^{c'}$), 1.5 (m, H$^{d'}$). ^{13}C NMR ($CDCl_3$): δ 180 (C^2), 133 (C^6), 135 (C^4), 154 (C^3), 120 (C^5), 24 (C$^{e'}$), 35 (C$^{d'}$), 21 (C$^{c'}$), 17 (C$^{b'}$), −1 (C$^{a'}$).

3,6-Bis(thexyldimethylsilyl)pyridine-2-thione. Anal. Calc. for $C_{21}H_{41}NSSi_2$: C, 63.73; H, 10.44; N, 3.54; S, 8.10. Found: C, 63.29; H, 10.21; N, 3.62; S, 8.42%. IR (KBr, cm^{-1}): 3160 (s), 3060 (w), 3030 (w), 2953 (vs), 1555 (vs), 1530 (s), 1460 (s), 1400 (w), 1380 (w), 1370 (m), 1310 (w), 1285 (vs), 1260 (w), 1245 (m), 1235 (m), 1155 (s), 1135 (vs), 1100 (m), 1030 (s), 990 (w), 880 (m), 830 (m), 815 (vs), 780 (m), 755 (m). ^{1}H NMR ($CDCl_3$): δ 13.6 (s, NH), 7.4 (d, H^4), 6.7 (d, H^5), 0.35 (s, H^a), 0.45 (s, H$^{a'}$), 0.85 (s, H^b), 0.95 (s, H$^{b'}$), 0.7 (d, H^c), 0.8 (d, H$^{c'}$), 1.5 (m, H^d), 1.7 (m, H$^{d'}$). ^{13}C NMR ($CDCl_3$): δ 185 (C^2), 145 (C^6), 154 (C^4), 144 (C^3), 119 (C^5), 24 (C^e), 25 (C$^{e'}$), 34 (C^d), 35 (C$^{d'}$), 21 (C^c), 22 (C$^{c'}$), 18 (C^b), 18 (C$^{b'}$), −5 (C^a), −2 (C$^{a'}$).

Synthesis of 3-(*tert*-butyldimethylsilyl)pyridine-2-thione. Although this compound had been prepared previously,[10,11] in both cases the yield was very low. However, the yield is *ca.* 85% if this material is prepared using the following method: 3,6-bis(*tert*-butyldimethylsilyl)pyridine-2-thione (3.5 g, 10.31 mmol in 90 ml of dry THF) was treated with a solution of tetrabutylammonium fluoride in THF (12.4 ml, 12.38 mmol, 1 M). A precipitate is formed immediately which dissolves in a few minutes. Water (100 ml) was added slowly to the solution and then treated with diethyl ether (100 ml). The ether layer was washed with water (100 ml), and the aqueous phase extracted with diethyl ether (3 × 35 ml). The organic phase was dried with Na_2SO_4, and concentrated *in vacuo* to give 3.3 g of crude product. Yield after recrystallization from hexane solution was 85% (2.99 g). Anal. Calc. for $C_{11}H_{19}NSSi$: C, 58.61; H, 8.50; N, 6.21; S, 14.22. Found: C, 58.29; H, 8.21; N, 6.62; S, 14.42%. IR (KBr, cm^{-1}): 3136 (m), 3068 (m), 3034 (m), 2925 (m), 1604 (s), 1570 (s), 1550 (s), 1467 (m), 1427 (m), 1411 (w), 1361 (w), 1303 (s), 1259 (m), 1242 (s), 955 (w), 935 (w), 886 (m), 825 (vs), 771 (vs), 763 (vs), 742 (w), 725 (m), 660 (s). ^{1}H NMR ($CDCl_3$): δ 13.9 (s, NH), 7.6 (d, H^4), 6.7 (dd, H^5), 7.5 (d, H^6), 0.42 (s, H^a), 1.0 (s, H^b). ^{13}C NMR ($CDCl_3$): δ 182 (C^2), 147 (C^6), 137 (C^4), 143 (C^3), 113 (C^5), 28 (C^b), 18 (C^c), −4 (C^a).

Preparation of the complexes

Electrochemical synthesis. The complexes were obtained using an electrochemical procedure. An acetonitrile solution of the ligand (50 ml) containing about 10 mg of tetramethylammonium perchlorate as a current carrier was electrolysed using a platinum wire as the cathode and a metal plate as the sacrificial anode. For the synthesis of the mixed complexes, the coligand was also added to the solution. Applied voltages of 10–15 V allowed sufficient current flow for smooth dissolution of the metal. As the electrolysis proceeded the colour of the solution changed, and hydrogen gas evolved from the cathode. The cells can be summarised as Pt(−)/CH_3CN + $RMe_2SipySH$ / M(+), where $RMe_2SipySH$ stands for the ligand.

The crystalline solids formed in the bottom of the cell were collected, washed with acetonitrile and diethyl ether and dried *in vacuo*. In some cases concentration of the resulting solution was required in order to obtain a solid product.

Synthesis of [3-Bu^{t}Me$_2$SipyS–Spy-3-Bu^{t}Me$_2$Si]. Following a similar procedure but using a tin foil anode suspended from a platinum wire and a solution of 3-(*tert*-butyldimethylsilyl)pyridine-2-thione in acetonitrile gives the ligand bis-3-(*tert*-butyldimethylsilyl)-2-pyridyl disulfide.

Synthesis of complexes [Ni(RMe$_2$SipyS)$_2$(bipy)]. For the synthesis of mixed complexes the corresponding coligand was added to the electrolytic phase. The cells can be summarised as: Pt(−)/CH_3CN + $RMe_2SipySH$ + L/Ni(+), L = bipyridine, phenanthroline. The solution compositions and experimental conditions are set out in Table 1 and the analytical data are given in Table 2.

Synthesis of phosphine containing complexes

[Cu(3-ThexMe$_2$SipyS)(dppm)]. To a solution of [Cu(3-ThexMe$_2$SipyS)] (0.087 g, 0.275 mmol) in acetonitrile (20 cm^3) was added a solution of dppm (0.105 g, 0.275 mmol) in the same solvent (25 cm^3). The reaction mixture was boiled for 48 h. The hot solution was filtered and allowed to evaporate to dryness at room temperature. A yellow solid was obtained and identified as [Cu(3-ThexMe$_2$SipyS)(dppm)]. Anal. Calc. for $C_{38}H_{44}$Cu-

Table 1 Experimental conditions for the electrochemical synthesis

Compound	Amount of ligand/g [a]	Initial voltage/V [b]	Time/h	Metal dissolved/mg	E_f/mol F^{-1}
[Co(3-Bu^{t}Me$_2$SipyS)$_3$]	0.166	20	2	22.0	0.50
[Co(3-ThexMe$_2$SipyS)$_3$]	0.188	20	2	21.0	0.48
[Co(6-ThexMe$_2$SipyS)$_3$]	0.188	20	2	22.5	0.52
[Ni(3-Bu^{t}Me$_2$SipyS)$_2$]	0.167	15	2	20.0	0.46
[Ni(3-Bu^{t}Me$_2$SipyS)$_2$(bipy)]	0.168	15	2	22.0	0.50
[Ni(3-ThexMe$_2$SipyS)$_2$]	0.188	15	2	21.0	0.48
[Ni(3-ThexMe$_2$SipyS)$_2$(bipy)]	0.170	15	2	22.5	0.51
[Ni(6-ThexMe$_2$SipyS)$_2$]	0.188	15	2	20.0	0.46
[Ni(6-ThexMe$_2$SipyS)$_2$(bipy)]	0.170	15	2	21.5	0.49
[Cu(3-Bu^{t}Me$_2$SipyS)]	0.170	20	2	47.0	0.99
[Cu(3-ThexMe$_2$SipyS)]	0.188	20	2	46.0	0.97
[Cu(6-ThexMe$_2$SipyS)]	0.192	20	2	46.0	0.97
[Ag(3-Bu^{t}Me$_2$SipyS)]	0.167	15	2	79.0	0.98
[Ag(3-ThexMe$_2$SipyS)]	0.187	15	2	76.0	0.94
[Ag(6-ThexMe$_2$SipyS)]	0.187	15	2	80.0	0.99

[a] Plus [NMe$_4$]ClO$_4$ (*ca.* 10 mg). [b] Voltage to produce a current of 10 mA.

Table 2 Analytical data for the complexes [a]

Compound	C (%)	N (%)	H (%)	S (%)
[Co(3-Bu^{t}Me$_2$SipyS)$_3$]	54.3 (54.1)	5.9 (5.7)	7.4 (7.4)	13.0 (13.1)
[Co(3-ThexMe$_2$SipyS)$_3$]	57.0 (57.4)	5.7 (5.1)	8.5 (8.1)	11.9 (11.8)
[Co(6-ThexMe$_2$SipyS)$_3$]	56.9 (57.4)	5.0 (5.1)	7.8 (8.1)	11.1 (11.8)
[Ni(3-Bu^{t}Me$_2$SipyS)$_2$]	51.8 (52.1)	5.5 (5.5)	7.1 (7.1)	12.6 (12.6)
[Ni(3-ThexMe$_2$SipyS)$_2$]	54.9 (55.4)	4.3 (4.9)	7.1 (7.9)	11.0 (11.4)
[Ni(6-ThexMe$_2$SipyS)$_2$]	54.9 (55.4)	4.8 (4.9)	7.4 (7.9)	11.2 (11.4)
[Ni(3-Bu^{t}Me$_2$SipyS)$_2$(bipy)]	57.6 (57.9)	8.1 (8.4)	7.0 (6.7)	9.9 (9.6)
[Ni(3-ThexMe$_2$SipyS)$_2$(bipy)]	59.8 (60.0)	7.5 (7.8)	7.5 (7.3)	8.3 (8.9)
[Ni(6-ThexMe$_2$SipyS)$_2$(bipy)]	59.6 (60.0)	7.3 (7.8)	7.4 (7.3)	8.6 (8.9)
[Cu(3-Bu^{t}Me$_2$SipyS)]·1/3CH$_3$CN	46.0 (46.5)	4.9 (6.2)	6.4 (6.4)	10.4 (10.6)
[Cu(3-ThexMe$_2$SipyS)]	49.5 (49.4)	4.9 (4.4)	6.4 (7.0)	10.4 (10.0)
[Cu(6-ThexMe$_2$SipyS)]	49.0 (49.4)	4.2 (4.4)	6.9 (7.0)	9.8 (10.0)
[Ag(3-Bu^{t}Me$_2$SipyS)]	39.9 (39.6)	4.3 (4.2)	5.9 (5.7)	9.6 (9.6)
[Ag(3-ThexMe$_2$SipyS)]	43.3 (43.2)	4.1 (3.9)	5.9 (6.1)	8.6 (8.9)
[Ag(6-ThexMe$_2$SipyS)]	43.2 (43.2)	4.1 (3.9)	5.8 (6.1)	8.8 (8.9)

[a] Calculated values are given in parentheses.

NP$_2$SSi: C, 65.1; N, 2.0; H, 6.3; S, 4.6. Found: C, 65.6; N, 1.9; H, 6.0; S, 4.3%. IR (KBr, cm^{-1}): 2955 (s), 1575 (s), 1550 (s), 1490 (s), 1470 (m), 1280 (s), 1260 (m), 1170 (vs), 1130 (s), 1100 (m), 1074 (m), 1025 (m), 835 (vs), 818 (vs), 780 (s), 750 (s), 700 (vs), 660 (m), 565 (m), 450 (m). ^{1}H NMR (CDCl$_3$): δ 7.6–7.3 (m, H^4, H^6 and the phenyl groups of the phosphine), 6.4 (t, H^5), 0.45 (s, H^a), 0.95 (s, H^b), 0.8 (d, H^c), 1.7 (m, H^d), 3.0 (s, CH$_2$). ^{13}C NMR (CDCl$_3$): δ 172 (C^2), 147 (C^6), 143 (C^3), 136–129 (C^4, C^5 and the aromatic dppm carbon atoms), 32 (C^e), 26 (C^d), 24 (C^c), 20 (C^b), −1 (C^a), 26.5 (CH$_2$).

[Cu(3-Bu^{t}Me$_2$SipyS)(dppm)]. A mixture of [Cu(3-Bu^{t}Me$_2$SipyS)] (0.062 g, 0.215 mmol) and dppm (0.082 g, 0.215 mmol) in acetonitrile (30 ml) was refluxed until a clear solution was obtained; concentration at room temperature afforded a yellow solid identified as [Cu(3-Bu^{t}Me$_2$SipyS)(dppm)]. Anal. Calc. for C$_{36}$H$_{40}$CuNP$_2$SSi: C, 64.3; N, 2.1; H, 6.0; S, 4.8. Found: C, 64.6; N, 1.9; H, 6.2; S, 5.0%. IR (KBr, cm^{-1}): 2950 (m), 2925 (m), 2892 (m), 1560 (s), 1540 (s), 1465 (m), 1362 (s), 1250 (m), 1230 (s), 1125 (s), 1030 (m), 886 (m), 832 (vs), 787 (vs), 763 (vs), 725 (s), 695 (vs), 680 (m). ^{1}H NMR (CDCl$_3$): δ 7.5–7.1 (m, H^4, H^5 and the phenyl groups of the phosphine), 6.35 (s, H^6), 0.40 (s, H^a), 0.95 (s, H^b), 3.2 (s, CH$_2$). ^{13}C NMR (CDCl$_3$): δ 171 (C^2), 146 (C^6), 132–129 (C^3, C^4 and the aromatic dppm carbon atoms), 113 (C^5), 29 (C^b), 18.5 (C^c), −2.5 (C^a), 26 (CH$_2$).

[Cu$_2$(3-Bu^{t}Me$_2$SipyS)$_2$(dppe)$_3$]. This compound was obtained by reacting [Cu(3-Bu^{t}Me$_2$SipyS)] (0.236 g, 0.594 mmol) and dppe (0.114 g, 0.396 mmol) in acetonitrile. This mixture was refluxed for 24 hours. Concentration of the resultant solution by evaporation at room temperature afforded a solid identified as [Cu$_2$(3-Bu^{t}Me$_2$SipyS)$_2$(dppe)$_3$]. Anal. Calc. for C$_{100}$H$_{110}$Cu$_2$N$_2$P$_6$S$_2$: C, 67.7; N, 1.6; H, 6.1; S, 3.6. Found: C, 67.6; N, 1.6; H, 5.7; S, 3.6%. IR (KBr, cm^{-1}): 2945 (m), 2920 (m), 1570 (s), 1550 (s), 1485 (m), 1440 (m), 1370 (s), 1295 (s), 1250 (m), 1240 (s), 1150 (m), 1030 (m), 955 (w), 880 (m), 835 (vs), 771 (vs), 750 (vs), 725 (m), 705 (vs), 660 (s). ^{1}H NMR (CDCl$_3$): δ 7.6–7.1 (m, H^4, H^5 and the phenyl groups of the phosphine), 6.5 (s, H^6), 0.45 (s, H^a), 1.0 (s, H^b), 2.3, 2.0 (CH$_2$). ^{13}C NMR (CDCl$_3$): δ 171 (C^2), 147 (C^6), 135–127 (C^3, C^4 and the aromatic dppe carbon atoms), 112 (C^5), 28.4 (C^b), 18 (C^c), −2.5 (C^a), 25.7 and 26.8 for (CH$_2$).

X-Ray crystallography

Crystals of [Cu$_6$(3-Bu^{t}Me$_2$SipyS)$_6$] and (3-Bu^{t}Me$_2$SipyS–Spy-3-Bu^{t}Me$_2$Si) were mounted on glass fibres on a Rigaku AFC5S diffractometer, while for [Cu$_6$(6-ThexMe$_2$SipyS)$_6$] a Siemens R3m/v diffractometer was used. Mo-Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator) at low temperature was used to collect the intensity data using the $2\theta/\omega$-scan technique. Three standard reflections monitored every 100 or 150 reflections showed no significant variation.

The crystallographic program system was the Siemens SHELXTL PLUS (PC version).[12] The structures were solved by direct methods and refined by a full matrix least-squares procedure. In the final cycles of the refinement, hydrogen atoms placed at idealised positions were included. The function minimised was $\Sigma w(F_o - F_c)^2$, where F_o and F_c are observed and calculated structure factors. Weighting schemes were of the form $w^{-1} = \sigma^2(F) + 0.0001\,F^2$. Neutral atom scattering factors were taken from Cromer and Waber.[13] Anomalous dispersion effects were those of Cromer.[14] The crystal data and summary of data collection and structure refinement for these compounds are given in Table 3. Significant bond distances and angles for **1**, **2** and **3** are given in Tables 4–6. ORTEP[35] diagrams of the molecules are shown in Figs. 1, 2 and 3.

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Results and discussion

Ligand synthesis

The ligands were obtained following a slightly modified version of Block's method (Scheme 1). In the case of these bulky substituents, the reaction leads to a mixture of different compounds, which could be separated by flash chromatography. It is worth noting that the amount of compound monosubstituted in the 3-position decreases as the bulkiness of the substituent increases (Scheme 1), a result also observed by Block and co-workers.[15] For that reason, the method is not good for the synthesis of derivatives with bulky substituents in the 3-position. Consequently, another method for their preparation was developed starting from the 3,6-disubstituted compound. It has been found that the substituent in the 6-position could be selectively cleaved if the 3,6-disubstituted compound was treated with tetrabutylammonium fluoride in THF (Scheme 2). When the reaction time in step (ii) (Scheme 3) is reduced from 12 to 2 hours the derivative with the substituent in the 6-position is produced almost exclusively, with a yield of 89%.

Synthesis of the metallic complexes

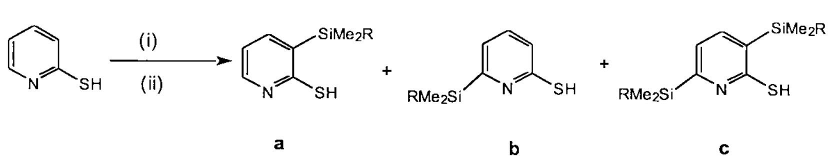
The electrochemical oxidation of a sacrificial metal anode (Co, Ni, Cu, Ag) in an acetonitrile solution of substituted thione, RMe$_2$SipySH, (3-ThexMe$_2$SipySH, 6-ThexMe$_2$SipySH or 3-Bu^{t}Me$_2$SipySH) proved to be a convenient one-step route to either [M(RMe$_2$SipyS)] (M = Cu, Ag) or [M(RMe$_2$SipyS)$_n$] (when M = Co, $n = 3$; M = Ni, $n = 2$).

Attempts have been made to prepare adducts of these

Table 3 Summary of crystal data, data collection and structure refinement for [Cu_6(3-Bu^{t}Me$_2$SipyS)$_6$] **1**, [Cu_6(6-ThexMe$_2$SipyS)$_6$] **2** and [3-Bu^{t}Me$_2$SipyS–Spy-3-Bu^{t}SiMe$_2$] **3**

	1	**2**	**3**
Empirical formula	$C_{35}H_{57}Cu_3N_4S_3Si_3$	$C_{13}H_{22}CuNSSi$	$C_{22}H_{36}N_2S_2Si_2$
Formula weight	904.9	316.0	448.8
Crystal system	Monoclinic	Trigonal	Triclinic
Space group	$C2/c$	P-(3)1c	P-(1)
a/Å	26.657(5)	17.693(3)	11.238(2)
b/Å	15.978(3)		14.161(3)
c/Å	24.895(5)	18.864(4)	8.264(2)
α/°			100.22(3)
β/°	120.27(3)		94.18(3)
γ/°			82.61(3)
V/Å^3	9157(5)	5114(3)	1281.8(6)
Z	8	12	2
μ(Mo-Kα)/mm^{-1}	1.623	1.459	0.312
T/K	253	253	213
No. of reflections collected	11015	4815	3343
No. of independent reflections	10754	2332	3343
R^a (%)	6.40	8.54	3.73
$R_w{}^b$ (%)	6.01	10.42	4.57

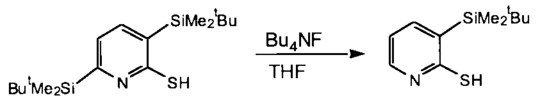
^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.



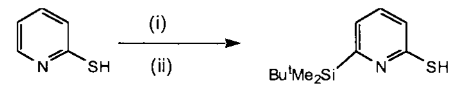
(i) LDA; (ii) ClSiMe$_2$R

	a	b	c
R= ^{t}Bu	3%	31%	33%
R=Thex	11.7%	13.4%	20.6%

Scheme 1



Scheme 2



(i) LDA; (ii) ClSiMe$_2$^{t}Bu, 2 h

Scheme 3

compounds in one-step by adding 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) as coligands into the cell. These experiments were unsuccessful except in the case of nickel where [Ni(RMe$_2$SipyS)$_2$(bipy)] was obtained.

The same negative result is observed when bidentate phosphines such as bis(diphenylphosphine)methane (dppm) and 1,2-bis(diphenylphosphine)ethane (dppe) are added to the cell. For this reason, the synthesis of the copper and silver mixed ligand complexes was attempted by reacting the phosphine ligand with the previously electrochemically synthesized copper or silver homoleptic complexes. In the case of silver, the analytical data show that no phosphine coordinates to the metal. However, in the case of copper [Cu$_2$(RMe$_2$SipyS)$_2$(dppe)$_3$] and [Cu$_2$(RMe$_2$SipyS)$_2$(dppm)$_2$] were isolated.

For copper and silver, the electrochemical efficiency E_f was always close to 1 mol F^{-1}. This is compatible with the following mechanism:

$$\text{Cathode: } RMe_2SipySH + 1e^- \rightarrow 1/2\ H_{2(g)} + RMe_2SipyS^-$$

$$\text{Anode: } RMe_2SipyS^- + M\ (Cu, Ag) \rightarrow [M(RMe_2SipyS)] + 1e^-$$

For Ni, E_f was close to 0.5 mol F^{-1}, that is compatible with:

$$\text{Cathode: } 2(RMe_2SipySH) + 2e^- \rightarrow H_{2(g)} + 2(RMe_2SipyS^-)$$

$$\text{Anode: } 2(RMe_2SipyS^-) + Ni \rightarrow [Ni(RMe_2SipyS)_2] + 2e^-$$

or

$$2(RMe_2SipyS^-) + Ni + bipy \rightarrow [Ni(RMe_2SipyS)_2(bipy)] + 2e^-$$

Values of E_f close to 0.5 mol F^{-1} were also found in the synthesis of cobalt complexes and are indicative of a similar anodic oxidation mechanism. However, the analytical data show that their composition is [Co(RMe$_2$SipyS)$_3$]. This observation suggests that the ligand oxidises the [Co(RMe$_2$SipyS)$_2$] as soon as this is formed.

$$[Co(RMe_2SipyS)_2] + RMe_2SipySH \longrightarrow [Co(RMe_2SipyS)_3] + \tfrac{1}{2}H_2$$

This behaviour has been previously observed in the synthesis of other cobalt complexes *via* an electrochemical procedure.[16]

Crystal structures

Molecular structure of [3-Bu^{t}Me$_2$SipyS–Spy-3-Bu^{t}SiMe$_2$] 3. A perspective view of **3** is shown in Fig. 1; selected bond lengths and angles are given in Table 4. The torsion angle C(1)S(1)-

Table 4 Bond lengths (Å) and angles (°) for [3-Bu^tMe_2SipyS–Spy-3-Bu^tMe_2Si] **3**

S(1)–S(2)	2.012(1)	S(1)–C(1)	1.789(3)
N(1)–C(1)	1.326(4)	N(1)–C(5)	1.333(4)
N(2)–C(12)	1.327(5)	N(2)–C(16)	1.334(5)
C(1)–C(2)	1.419(4)	C(2)–C(3)	1.380(4)
C(3)–C(4)	1.379(5)	C(4)–C(5)	1.370(5)
C(12)–C(13)	1.403(5)	C(13)–C(14)	1.387(5)
C(14)–C(15)	1.386(6)	C(15)–C(16)	1.366(5)
S(2)–S(1)–C(1)	104.8(1)	S(1)–S(2)–C(12)	105.2(1)
C(1)–N(1)–C(5)	117.2(3)	C(12)–N(2)–C(16)	116.9(3)
S(1)–C(1)–N(1)	116.8(2)	S(1)–C(1)–C(2)	117.7(2)
N(1)–C(1)–C(2)	125.4(3)	C(1)–C(2)–C(3)	113.6(3)
C(2)–C(3)–C(4)	122.6(3)	C(3)–C(4)–C(5)	117.5(3)
N(1)–C(5)–C(4)	123.6(3)	S(2)–C(12)–N(2)	116.8(2)
S(2)–C(12)–C(13)	117.4(3)	N(2)–C(12)–C(13)	125.8(3)
C(12)–C(13)–C(14)	114.0(3)	C(13)–C(14)–C(15)	121.9(3)
C(14)–C(15)–C(16)	117.5(4)	N(2)–C(16)–C(15)	123.8(4)

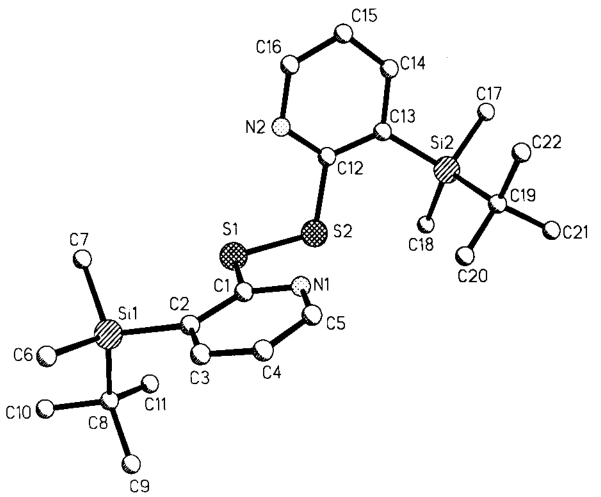


Fig. 1 The molecular structure of [3-Bu^tMe_2SipyS–Spy-3-Bu^tMe_2Si] **3**.

S(2)C(12) of *ca.* 89.6(4)° is within the range usually found in most aromatic disulfides (90 ± 10°). Furthermore, the torsion angles X–C–S–S, where X = N or C, (N(1)C(1)S(1)S(2) 10.7(5); N(2)C(12)S(2)S(1) −7.3(4), C(2)C(1)S(1)S(2) 170.3(7)° and C(13)C(12)S(2)S(1) 174.5(7)°) are close to 0 or 180°, and within the range found in other substituted aromatic disulfides with an equatorial conformation, according to the Shefter classification[17] (*ca.* 0 or 180° equatorial and 90° axial conformations). This means that both sulfur atoms lie approximately in the plane of the pyridine ring to which they are bound (by 0.049 for S(1) and 0.059 Å for S(2)). The average S–C distance, 1.794(3) Å, is likewise similar to those observed in other organic disulfides with an equatorial conformation[18] and is consistent with a single S–C bond. In addition and in accordance with the equatorial conformation, the S–S bond distance, 2.012(1) Å, is shorter and the C–S–S angles, 104.8(1) and 105.2(1)°, larger than in other unsubstituted organic disulfides which show an axial conformation (2.060–2.108 Å and 100–103°).[18,19]

The pyridine rings are effectively planar; the maximum deviation from a least squares plane is 0.009 Å, with bond lengths and angles similar to those observed in other pyridine derivatives. The angles N(1)–C(1)–C(2) and N(2)–C(12)–C(13) are larger (125.4(3) and 125.8(3)°, respectively) than in pyridine-2-thione (115.2(2)°)[20] with both pyridine rings almost perpendicular, interplanar angle 90.02(6)°.

The Si(1) atom lies approximately on the plane of the pyridine ring to which it is bound (0.012(2) Å). The other Si atom is out of the plane of the pyridine to which it is bound (0.071(1) Å). The *tert*-butyl groups are approximately perpendicular to the pyridine ring to which they are bound, 81.19(7) and 90.10(9)° respectively whereas the dihedral angle between them is only 59.58(9)°.

Table 5 Selected bond lengths (Å) and angles (°) for [Cu_6(3-Bu^tMe_2-SipyS)$_6$] **1**

Cu(1)–Cu(2)	2.695(3)	Cu(1)–Cu(3)	2.974(3)
Cu(1)–S(1)	2.231(4)	Cu(1)–S(2)	2.271(5)
Cu(1)–Cu(3A)	2.875(3)	Cu(1)–N(3A)	2.025(12)
Cu(2)–Cu(3)	2.800(2)	Cu(2)–N(1)	2.010(15)
Cu(2)–S(2A)	2.267(5)	Cu(2)–S(3A)	2.229(4)
Cu(3)–S(1)	2.236(5)	Cu(3)–S(3)	2.249(5)
Cu(3)–Cu(1A)	2.875(3)	Cu(3)–N(2A)	2.032(12)
S(1)–C(1)	1.767(19)	S(2)–C(12)	1.772(15)
S(2)–Cu(2A)	2.267(5)	S(3)–C(23)	1.765(16)
S(3)–Cu(2A)	2.229(4)	N(1)–C(1)	1.353(16)
N(1)–C(5)	1.340(23)	N(2)–C(12)	1.357(15)
N(2)–C(16)	1.338(18)	N(2)–Cu(3A)	2.032(12)
N(3)–C(23)	1.348(15)	N(3)–C(27)	1.337(21)
N(3)–Cu(1A)	2.025(12)		
S(1)–Cu(1)–S(2)	115.8(2)	S(1)–Cu(1)–N(3A)	124.2(5)
S(2)–Cu(1)–N(3A)	111.0(4)	Cu(1)–Cu(2)–Cu(3)	65.5(1)
N(1)–Cu(2)–S(2A)	110.0(4)	Cu(1)–Cu(2)–S(3A)	77.3(1)
Cu(3)–Cu(2)–S(3A)	132.2(2)	S(2A)–Cu(2)–S(3A)	113.0(2)
S(1)–Cu(3)–S(3)	123.1(2)	Cu(1)–Cu(3)–Cu(1A)	92.2(1)
Cu(2)–Cu(3)–Cu(1A)	70.3(1)	S(1)–Cu(3)–N(2A)	117.0(5)
S(3)–Cu(3)–N(2A)	110.7(4)	Cu(1)–S(1)–Cu(3)	83.5(2)
Cu(1)–S(2)–Cu(2A)	92.1(2)	C(12)–S(2)–Cu(2A)	106.2(6)
Cu(2)–N(1)–C(5)	122.1(9)	C(1)–N(1)–C(5)	119.4(15)
C(12)–N(2)–C(16)	117.7(12)	C(12)–N(2)–Cu(3A)	121.1(9)
C(16)–N(2)–Cu(3A)	121.1(8)	C(23)–N(3)–C(27)	118.8(12)
C(23)–N(3)–Cu(1A)	117.9(10)	C(27)–N(3)–Cu(1A)	122.3(8)

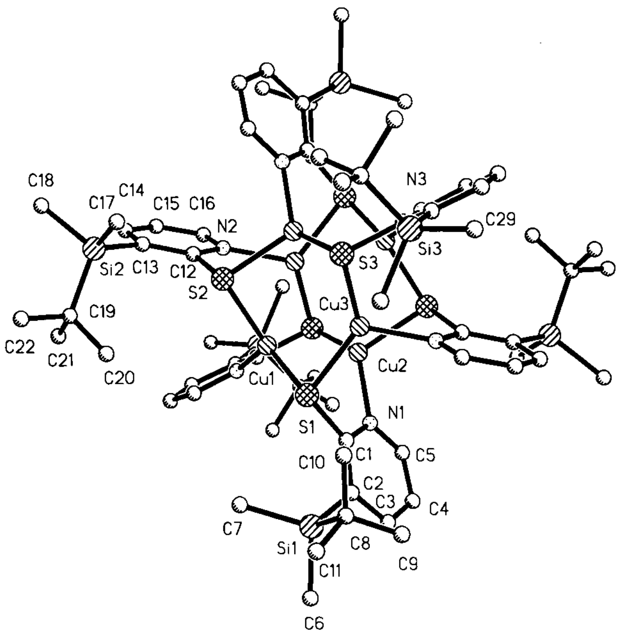


Fig. 2 The molecular structure of [Cu_6(3-Bu^tMe_2SipyS)$_6$] **1**.

Molecular structure of [Cu_6(3-Bu^tMe_2SipyS)$_6$] 1. Fig. 2 shows a perspective view of the molecular structure of **1** with the atom labelling scheme used. Selected bond distances and angles with estimated standard deviations are given in Table 5.

The structure of **1** consists of discrete neutral hexanuclear units containing a cluster of six copper atoms. This cluster is significantly distorted from octahedral symmetry with individual copper–copper distances in the range 2.695(3)–3.267(5) Å. Thus, the octahedron defined by the six copper atoms has four large triangular faces of approximately isosceles habit and four smaller ones, of which two are approximately isosceles triangular faces and the others are scalene. All the copper–copper distances are considerably greater than the distance in metallic copper, 2.40 Å,[21] showing that no significant metal–metal interaction exists.

Each copper atom is coordinated to one nitrogen atom of one thionate ligand and to two bridging sulfur atoms of two ligands bound to two other copper atoms. Therefore, each ligand acts as a bridging μ_3(N,S) five electron donor on the three copper atoms which define a face of the octahedron. Each copper atom is in a distorted trigonal environment [CuS_2N] as a consequence of the inequivalence of the donor atoms in the CuS_2N core, causing the copper atom to move away from the plane formed by the donor atoms (0.36 to 0.38 Å) and the values of the angles around the copper atom (110.0(4) to 128.3(4)°), to deviate considerably from the ideal value.

The Cu–S bond distances, 2.229(4)–2.271(5) Å, are very similar to those found in other hexanuclear complexes of copper(I) with derivatives of pyridine-2-thione and pyrimidine-2-thione,[22–24] in which the copper atom is also three-coordinate with a distorted trigonal planar environment. The Cu–N distances, 2.010(15)–2.032(12) Å, are likewise similar to those observed in the above mentioned thionate copper(I) complexes.

The pyridine rings are essentially planar, with the S(3) atom lying approximately in the plane (0.025 Å) of the pyridine ring to which it is bound, but the other sulfur atoms lie out of the plane of the pyridine ring [by 0.231 for S(1) and 0.182 for S(2)]. The average S–C and C–N, bond distances, 1.768(17) and 1.345(16) Å, respectively, are intermediate to the value observed in free pyridine-2-thione (1.695(2) Å, 1.356(3) Å, respectively),[25] and in bis-3(*tert*-butyldimethylsilyl)-2-pyridyl disulfide (average C–S, 1.794(3) Å and average N–C, 1.330(5) Å), suggesting that the ligand is coordinating in a form that is closer to pyridine-2-thionato than to the thione form.

The metal cluster and acetonitrile molecules are separated by normal van der Waals distances and there are no abnormally short intermolecular contacts. It should be emphasised that the acetonitrile molecule is not incorporated into any copper atom coordination sphere.

Molecular structure of [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] 2. A perspective view of the molecular structure of **2** with the atom labelling scheme is illustrated in Fig. 3. Selected bond distances and angles with estimated standard deviations are given in Table 6.

The structure of [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] shows again a distorted octahedral disposition of six copper atoms. This distortion is smaller than that found for [$Cu_6(3\text{-Bu}^t\text{Me}_2\text{SipyS})_6$] and is characterised by two opposite triangular faces being significantly larger than the remaining ones. The Cu–Cu distances within these larger faces are 3.608 Å. The Cu–Cu distances observed for the smaller faces are in the range 3.608(9)–2.701(10) Å. Once again, no significant copper–copper interaction exists in the compound.

Table 7 summarises the structural information available for hexanuclear copper(I) compounds with derivatives of pyridine-2-thione or pyrimidine-2-thione. In spite of some obvious similarities in the Cu_6 core structures, it should be noted that there are significant differences between [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] and the other complexes. Thus, if the structure is described as two Cu_3S_3 rings in a *gauche* disposition, in [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] the copper atoms of each ring form an equilateral triangular face with copper–copper distances of 3.608 Å, whereas in the other complexes the Cu–Cu distances in each ring are different and smaller (range 3.433(2)–3.139(1) Å) than in [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$]. Therefore, the ring Cu_3S_3 geometry in [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] is much more regular than those of [$Cu_6(3\text{-Bu}^t\text{Me}_2\text{SipyS})_6$] and of other previously reported examples. This is probably the result of the angular relaxation allowed by the increased ring size. One consequence of this observation is the expansion of the Cu–S–Cu angle and a reduction in the S–Cu–S angle in [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] in comparison with the values for the corresponding angles in the other complexes.

Table 6 Bond lengths (Å) and angles (°) for [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] **2**

Cu(1)–S(1)	2.218(15)	Cu(1)–N(1)	2.054(36)
Cu(1)–Cu(1B)	3.037(8)	Cu(1)–Cu(1C)	2.701(10)
Cu(1)–S(1A)	2.308(10)	S(1)–Cu(1A)	2.308(13)
S(1)–C(1A)	1.737(29)	N(1)–C(1)	1.447(38)
N(1)–C(5)	1.271(61)	C(1)–C(2)	1.393(63)
C(1)–S(1B)	1.737(45)	C(2)–C(3)	1.283(75)
C(3)–C(4)	1.363(61)	C(4)–C(5)	1.401(74)
S(1)–Cu(1)–N(1)	138.8(7)	S(1)–Cu(1)–S(1A)	107.0(6)
N(1)–Cu(1)–S(1A)	110.0(8)	Cu(1)–S(1)–Cu(1A)	105.7(4)
Cu(1)–S(1)–C(1A)	112.7(15)	Cu(1A)–S(1)–C(1A)	100.1(15)
Cu(1)–N(1)–C(1)	101.6(26)	Cu(1)–N(1)–C(5)	138.6(23)
C(1)–N(1)–C(5)	119.7(34)	N(1)–C(1)–C(2)	117.7(38)
N(1)–C(1)–S(1B)	122.3(30)	C(2)–C(1)–S(1B)	120.0(26)
C(1)–C(2)–C(3)	118.7(38)	C(2)–C(3)–C(4)	124.7(52)
C(3)–C(4)–C(5)	116.3(53)	N(1)–C(5)–C(4)	121.9(35)

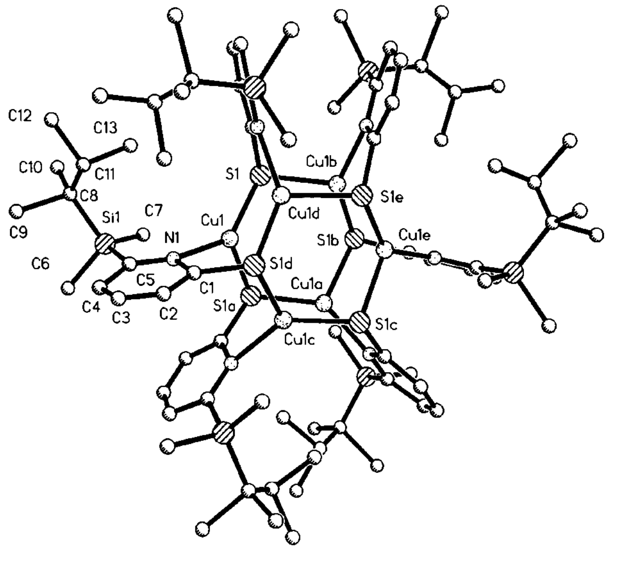


Fig. 3 The molecular structure of [$Cu_6(6\text{-ThexMe}_2\text{SipyS})_6$] **2**.

The coordination geometry around the Cu atom is highly distorted trigonal as is illustrated by the values of the angles around the Cu atom which range from 107.0(6) to 138.8(7)°. The copper atom is nearly 0.25 Å out of the plane formed by the donor atoms.

As in [$Cu_6(3\text{-Bu}^t\text{Me}_2\text{SipyS})_6$] each ligand is bonded to three different copper atoms defining a face of the octahedron with the sulfur atom bridging two metal atoms while each copper atom is bound to three ligands (to two *via* sulfur atoms and to one *via* a nitrogen atom).

The bridging sulfur atom has one Cu–S bond slightly longer than the other, [Cu(1)–S(1), 2.218(15); Cu(1)–S(1A), 2.308(10) Å] and both are similar to the corresponding values found in [$Cu_6(3\text{-Bu}^t\text{Me}_2\text{SipyS})_6$] and in the above mentioned hexanuclear copper complexes. The Cu–N distance, 2.054(36) Å, is similar to those observed in other hexanuclear thionato copper(I) complexes.

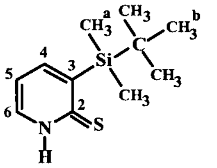
The pyridine rings are essentially planar, with the S and Si atoms lying approximately in the plane (0.012 and 0.014 Å, respectively) of the pyridine ring to which they are bound. The S–C bond distance, 1.737(29) Å, is similar to those found in other thiolato copper complexes.

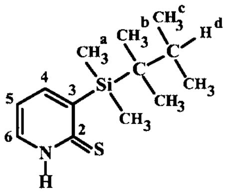
It is apparent from the structures of **1** and **2** and from previously reported examples of [$Cu_6(NS)_6$] structural types, that the steric demands of the substituents in these thionato ligands do not provide sufficient steric congestion to reduce the degree of association in these copper(I) complexes. However, the size of the Cu_3S_3 ring appears to depend on the steric demand imposed by the ligand.

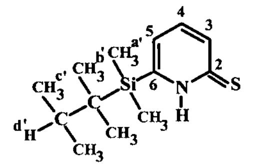
Table 7 Comparison of bond lengths (Å) and angles (°) for hexanuclear copper(I) compounds with derivatives of pyridine-2-thione or pyrimidine-2-thione

Compounds	Cu–Cu distance shortest/longest	Cu–S	Cu–N	S–Cu–S	S–Cu–N	Cu–S–Cu	S–C	Ref.
$[Cu_6(pyS)_6]$	2.795(1)/3.160(1)	2.238(2)	2.030(7)	115.89(8) 122.3(2)	109.7(2) 124.8(2)	89.1 85.7 85.0	1.751(7) 1.777(8)	22
$[Cu_6(3\text{-}Me_3SipyS)_6]$	2.961(3)/3.139(1)	2.245(2)	2.034(7)	119.2(2) 113.3(1)	112.1(2) 119.2(2)	82.6(1) 88.5(1)	1.751(7) 1.777(8)	23
$[Cu_6(4,6\text{-}Me_2pymS)_6]$	2.711(2)/3.433(2)	2.212(3) 2.279(3)	2.022(8)	105.6(1) 122.2(1)	106.0(2) 133.0(2)	87.9(1) 82.34	1.76(1)	24
$[Cu_6(6\text{-}ThexMe_2SipyS)_6]$	2.701(10)/3.608(9)	2.218(15) 2.308(10)	2.054(36)	107.0(6)	110.0(8) 138.8(7)	105.7(4)	1.737(29)	This work
$[Cu_6(3\text{-}Bu^tMe_2SipyS)_6]$	2.695(3)/3.267(5)	2.229(4) 2.271(5) 2.267(5) 2.249(5) 2.236(5)	2.010(15) 2.032(12) 2.025(12)	113.0(2) 123.1(2) 115.8(2)	110.7(4) 128.3(4) 124.2(5) 111.0(4) 117.0(5)	83.5(2) 92.1(2) 86.6(2)	1.772(15) 1.765(16) 1.767(19)	This work

Table 8 ^1H NMR (ppm) for the complexes







Compound	H^3	H^4	H^5	H^6	H^a	$H^{a'}$	H^b	$H^{b'}$	H^c	$H^{c'}$	H^d	$H^{d'}$
$[Co(3\text{-}Bu^tMe_2SipyS)_3]$		7.6d	7.5m	6.6m	0.4s		0.9s					
$[Co(3\text{-}ThexMe_2SipyS)_3]$		7.4d	7.2d	7.7d	0.22		0.9s		0.75		1.2m	
$[Co(6\text{-}ThexMe_2SipyS)_3]$	7.8	7.5d	7.1			0.50		0.98		0.83		1.8m
$[Ni(3\text{-}Bu^tMe_2SipyS)_2]$		7.4t	7.0	6.45s	0.4s		1.0s					
$[Ni(3\text{-}ThexMe_2SipyS)_2]$		6.7d	6.3d	7.2d	0.2s		0.7s		0.6s		1.5m	
$[Cu(3\text{-}Bu^tMe_2SipyS)]$		7.64s	7.19m	6.40s	0.41s		0.95s					
$[Cu(3\text{-}ThexMe_2SipyS)]$		7.1d	6.3t	7.6d	0.4s		0.9s		0.7d		1.7m	
$[Cu(6\text{-}ThexMe_2SipyS)]$	7.40	7.1	6.9			0.30		1.15		0.7		1.7m
$[Ag(3\text{-}Bu^tMe_2pyS)]$		7.82s	6.55m	6.85s	0.43m		0.98s					
$[Ag(3\text{-}ThexMe_2SipyS)]$		7.4d	6.4t	7.8d	0.4s		0.9s		0.7d		1.7m	
$[Ag(6\text{-}ThexMe_2SipyS)]$	7.45	7.0	6.8			0.30		1.35		0.5		1.8m

Vibrational spectra

The IR spectra of the complexes show no bands assignable to ν(N–H) (3180–3100 cm^{-1} for the free ligands), suggesting that deprotonation of the NH group has occurred during the electrosynthesis and therefore that the ligand is coordinated in the thionato form.

The strong bands for ν(C=C) and ν(C=N) at 1604–1545 and 1570–1512 cm^{-1} in the free ligands spectra are shifted to smaller wavenumbers in their complexes. This is further confirmation that the ligand is coordinated in the thionato form. All the IR spectra show a strong band between 825–810 cm^{-1} which can be attributed to ν(C–Si).[26]

The mixed-ligand complexes show IR absorption bands of coordinated bipyridine (*ca.* 770 and 740 cm^{-1})[27] and coordinated dppm (*ca.* 1470 (m), 1130 (s), 1025 (m), 785 (s), 725 (s) and 700 (vs) cm^{-1}) or coordinated dppe (*ca.* 1440 (m), 1150 (m), 1030 (m), 750 (s) and 705 (vs) cm^{-1}).[28]

NMR spectra

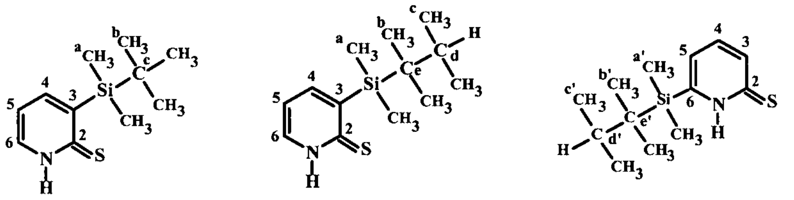
The ^1H and ^{13}C NMR spectra of the free ligands were assigned through COSY $^1H/^{13}C$ experiments. The ^1H NMR spectra of the complexes (Table 8) do not show the signal attributable to the NH proton of the free ligand, which appears as a broad singlet between 13.0 and 14.0 ppm, proving that in the complexes the ligands are deprotonated. The spectra show the signals of all the hydrogen atoms of the pyridine ring and methyl shifted with respect to the corresponding signals in the free ligand spectra. The ^{13}C NMR spectra of the complexes (Table 9) show all the expected signals and the main change observed is the upfield shift of C_2 probably due to the reduction in the order of the C–S bond.[29] This is further evidence of the predominance of the thionato form of the ligand in the complexes.

The similarity of the NMR spectra of all silver and copper compounds led us to suggest that these compounds have a similar structure. Therefore a hexanuclear structure for $[Cu(RMe_2SipyS)]$ and $[Ag(RMe_2SipyS)]$, similar to that found by X-ray diffraction in the case of $[Cu(3\text{-}Bu^tMe_2SipyS)]_6$ and $[Cu(6\text{-}ThexMe_2SipyS)]_6$, *vide supra*, and for $[Ag(6\text{-}Bu^tMe_2SipyS)]_6$,[30] is proposed for all of them.

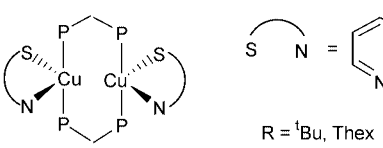
The ^1H NMR spectra of the complexes $[Cu_2(RMe_2SipyS)_2(dppm)_2]$ show in addition to the signals corresponding to the hydrogen atoms of the thionate heterocyclic ligand, a multiplet in the aromatic region and a singlet at *ca.* 3 ppm, that are attributable to the phenyl and methylene protons of the dppm ligand, respectively. The ^{13}C spectra of $[Cu_2(RMe_2SipyS)_2(dppm)_2]$ show resonances in the aromatic region and a signal at *ca.* 26.7 ppm assignable to the phenyl and methylene carbons of dppm, respectively. These data are very similar to those of the $[Cu_2(6\text{-}Bu^tMe_2SipyS)_2(dppm)_2]$ complex[31] and therefore it is reasonable to assume that the complexes $[Cu_2(RMe_2SipyS)_2(dppm)_2]$ have a similar dimeric structure as shown below.

The ^1H NMR spectrum of the complex $[Cu_2(3\text{-}Bu^tMe_2\text{-}$

Table 9 ^{13}C NMR (ppm) for the complexes



Compound	C^2	C^6	C^3	C^4	C^5	C^e	C$^{e'}$	C^d	C$^{d'}$	C^c	C$^{c'}$	C^b	C$^{b'}$	C^a	C$^{a'}$
[Co(3-$\mathrm{Bu^tMe_2SipyS)_3}$]		168	150	134	116					18		27		−3	
[Co(3-$\mathrm{ThexMe_2SipyS)_3}$]	172	150	142	137	126	34		25		22		19		−2	
[Co(6-$\mathrm{ThexMe_2SipyS)_3}$]	179	170	149	131	125		35		25		22				−4
[Ni(3-$\mathrm{Bu^tMe_2SipyS)_2}$]	174	147	135	145	117					18		27		−5	
[Ni(3-$\mathrm{ThexMe_2SipyS)_2}$]	180	148	145	138	118		35		26		22		18		−3
[Cu(3-$\mathrm{Bu^tMe_2SipyS}$)]	172		116	133						19.0		28.2		−2.5	
[Cu(3-$\mathrm{ThexMe_2SipyS}$)]	175	150	143	136	117	36		26		24		20		−1	
[Cu(6-$\mathrm{ThexMe_2SipyS}$)]	172	148	135	126	115		35		25		22		19		−2.5
[Ag(3-$\mathrm{Bu^tMe_2pyS}$)]	165	150	127	134						18.5		27.0		−2.5	
[Ag(3-$\mathrm{ThexMe_2SipyS}$)]	175	149	143	136	117	35		26		24		20			
[Ag(6-$\mathrm{ThexMe_2pyS}$)]	172	145	133	127	112		35		24		21		19		−3



SipyS)$_2$(dppe)$_3$] also exhibits a multiplet in the aromatic region due to the phenyl hydrogen atoms of dppe and two signals due to the dppe methylene hydrogen at 2.3 and 2.0 ppm, suggesting the presence of two non-equivalent dppe ligands in this compound. The ^{13}C spectrum of [$\mathrm{Cu_2(3\text{-}Bu^tMe_2SipyS)_2(dppe)_3}$] shows additional resonances in the aromatic region at *ca.* 26.8 and 25.7 ppm due to the methylene carbon atoms of two non-equivalent dppe ligands. We therefore suggest that the complex probably has a dimeric structure with each copper atom tetrahedrally coordinated to one bridging dppe molecule, one chelating dppe molecule and a single S-monodentate thionato ligand (see Chart 1), as has been observed by X-ray diffraction in the case of [$\mathrm{Cu_2(3\text{-}Me_3SipyS)_2(dppe)_3}$].[32]

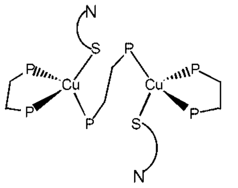


Chart 1

The ^{1}H NMR spectra of the [$\mathrm{Co(RMe_2SipyS)_3}$] complexes show only four signals for the hydrogen atoms of the pyridine rings and three signals for the methyl groups, indicating that the ligands in these complexes are chemically equivalent and therefore that these compounds in solution have a facial arrangement of the ligands. This is corroborated by the presence of only five signals for the carbon atoms of the pyridine rings and only three or four signals for the carbon atoms of the Bu^t or Thexyl substituent respectively in the ^{13}C NMR.

Magnetic moments and electronic spectra

The magnetic moments of the [$\mathrm{Co(RMe_2SipyS)_3}$] complexes show that these compounds are diamagnetic, as expected for low spin d^6 octahedral complexes. The solid state electronic spectra of these complexes show two bands in the 14300–14900 and 17200–18000 cm^{-1} ranges, as expected for low-spin six-coordinated cobalt(III) complexes. The first band is due to a $^1T_{1g}\leftarrow{}^1A_{1g}$ transition and the second to a $^1T_{2g}\leftarrow{}^1A_{1g}$ transition.[33] The [$\mathrm{Ni(RMe_2SipyS)_2}$] complexes also exhibit a diamagnetic behaviour, compatible with a square planar coordination around the metal. The diffuse reflectance spectra of [$\mathrm{Ni(RMe_2SipyS)_2}$] have three bands attributable to the transitions $^1A_{1g}\rightarrow{}^1B_{1g}$ (15700 cm^{-1}), $^1A_{1g}\rightarrow{}^1E_g$ (20800 cm^{-1}) and $^1A_{1g}\rightarrow{}^1A_{2g}$ (23250 cm^{-1}). These results are very similar to those found for [$\mathrm{Ni(3\text{-}Me_3SipyS)_2}$], for which a square planar structure has been confirmed by X-ray diffraction.[34]

The magnetic moments of the mixed nickel(II) complexes lie in the range 2.95–3.18 μ_B at room temperature. These values are of the order expected for octahedral nickel(II) complexes. The electronic spectral data for the [$\mathrm{Ni(RMe_2SipyS)_2(bipy)}$] complexes show bands at *ca.* 10860 cm^{-1} and 17760 cm^{-1}, and a shoulder at *ca.* 12580 cm^{-1}. These bands are also consistent with an octahedral environment around the nickel(II) ion and can be assigned to the transitions $^3A_{2g}\rightarrow{}^3T_{2g}(\nu_1)$ and $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) (ν_2), respectively.[33] The shoulder at *ca.* 12580 cm^{-1} can be considered as the result of the splitting of the first band as a consequence of the distortion from octahedral symmetry. The third expected d–d transition is presumably hidden under the strong charge-transfer band observed in the 20000–30000 cm^{-1} region.

These data support a square planar environment for the nickel atom in the [$\mathrm{Ni(RMe_2SipyS)_2}$] complexes and an octahedral environment around the metal for [$\mathrm{Co(RMe_2SipyS)_3}$] and [$\mathrm{Ni(RMe_2SipyS)_2(bipy)}$].

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