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Synthesis, Spectroscopy, and Structures of Mono- and Dinuclear Copper(I) Halide Complexes with 1,3-Imidazolidine-2-thiones

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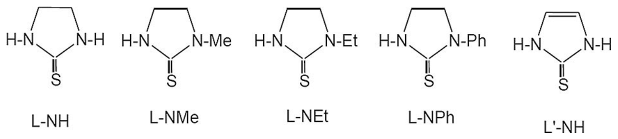
Abstract. Copper(I) halides with triphenyl phosphine and imidaozlidine-2-thiones (L-NMe, L-NEt, and L-NPh) in acetonitrile/methanol (or dichloromethane) yielded copper(I) mixed-ligand complexes: mononuclear, namely, $[CuCl(\kappa^1\text{-}S\text{-L-NMe})(PPh_3)_2]$ (**1**), $[CuBr(\kappa^1\text{-}S\text{-L-NMe})(PPh_3)_2]$ (**2**), $[CuBr(\kappa^1\text{-}S\text{-L-NEt})(PPh_3)_2]$ (**5**), $[CuI(\kappa^1\text{-}S\text{-L-NEt})(PPh_3)_2]$ (**6**), $[CuCl(\kappa^1\text{-}S\text{-L-NPh})(PPh_3)_2]$ (**7**), and $[CuBr(\kappa^1\text{-}S\text{-L-NPh})(PPh_3)_2]$ (**8**), and dinuclear, $[Cu_2(\kappa^1\text{-}I)_2(\mu\text{-}S\text{-L-NMe})_2(PPh_3)_2]$ (**3**) and $[Cu_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-L-NEt})_2(PPh_3)_2]$ (**4**). All complexes were characterized with analytical data, IR and NMR spectroscopy, and X-ray crystallography. Complexes **2**–**4**, **7**, and **8** each formed crystals in the triclinic system with $P\bar{1}$ space group, whereas complexes **1**, **5**, and **6** crystallized in the monoclinic crystal system with space groups $P2_1/c$, $C2/c$, and $P2_1/n$, respectively. Complex **2** has shown two independent molecules, $[(CuBr(\kappa^1\text{-}S\text{-L-NMe})(PPh_3)_2]$ and $[CuBr(PPh_3)_2]$ in the unit cell. For X = Cl, the thio-ligand bonded to metal as terminal in complex **4**, whereas for X = I it is sulfur-bridged in complex **3**.

Introduction

The chemistry of heterocyclic-2-thiones has invited interest of several researchers for a variety of reasons such as relevance of their metal complexes in the biological systems,[1,2] and versatility of these organic bases to bind to metals in different coordination patterns leading to the formation of a wide variety of coordination compounds, ranging from mono- to poly-nuclear.[3–18] Among heterocyclic-2-thiones, 1,3-imidazolidine-2-thione and its derivatives have been used for the investigation of their interaction with metals.[3–8] The ligands, 1,3-imidazolidine-2-thione and its derivatives with mono substitution at one nitrogen (L-N*R*, *R* = H, Me, Et, *n*Pr, iPr) with copper(I) halides / pseudo halides have yielded trigonal planar complexes, $[CuX(\text{L-NR})_2]$ (X = Cl, Br, I, NCS).[19–24] The double substitution at both nitrogen atoms $\{\text{L-(NMe)}_2\}$ also formed a similar three coordinate complex.[25] Dinuclear[26,27] or polynuclear[27,28] complexes of 1,3-imidazolidine-2-thiones with copper(I) halides are also reported. Several heterocyclic-2-thiones such as pyridine-2-thione, pyrimidine-2-thione, thiazolidine-2-thione etc. have formed mixed-ligand complexes such as, $[CuX(HL)(PPh_3)_2]$, with PPh_3 as co-ligand,[29–38] whereas no similar mixed-ligand complexes with imidazolidine-2-thiones are known.

We have observed that thio-ligand L-NH (Scheme 1) reacted with copper(I) chloride / bromide in dimethylsulfoxide (or DMF) and formed a sulfate bridged polymer, $[Cu^{II}\{\kappa^2\text{-}N,N\text{-}(N_2C_3H_5)_2S\}(\mu\text{-}O,OSO_2)(\kappa^1\text{-}OH_2)]_n$ [$(N_2C_3H_5)_2S$ = 2,2′-thio-di-2-imidazoline] involving C–S rupture.[39] Further reactions of L-NMe, L-NEt, and L-NPh with copper(I) chloride / bromide in acetonitrile, dimethylsulfoxide (or DMF) also involved C–S rupture but no product could be established except formation of copper(II) sulfate. In this paper, results of reactions of thio-ligands (L-N*R*, *R* = Me, Et, Ph) (Scheme 1) with copper(I) halides carried out in the presence of PPh_3 as co-ligand are reported. New mixed-ligand copper(I) mono- and dinuclear complexes **1**–**8** reported represent the first examples with imidazolidine-2-thiones.



Scheme 1. The imidazolidinethiones used as ligands.

Experimental Section

Materials and Techniques: The thio ligands, 1-methyl-imidazolidine-2-thione (L-NMe) was prepared by the addition of carbon disulphide dropwise to a cooled solution of 1-methyl-ethylenediamine in ethanol and water. The reaction mixture was heated under reflux (110 °C) for 1 h and conc. HCl was added. The mixture was heated under reflux

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for a further period of 10 h. The reaction mixture was cooled and stored in a freezer. The resulting precipitate were filtered off and washed with cold acetone to give the desired ligand. Similarly, 1-ethyl-imidazolidine-2-thione (L-NEt) and 1-phenyl-imidazolidine-2-thione (L-NPh) were prepared.[40] Copper(I) halides were prepared by the reduction of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of stoichiometric amounts of corresponding NaCl, NaBr, or NaI in water.[41] The melting point was determined with a Gallenkamp electrically heated apparatus. The IR spectra were recorded using KBr pellets with Varian 660 FT IR and Perkin-Elmer FT IR Spectrometer in the 4000–200 cm^{-1} range. The ^1H NMR spectra were recorded in $CDCl_3$ with a Bruker Avance II 400 NMR spectrometer at 400 MHz and JEOL AL300 FT ^1H NMR at 300 MHz using TMS as an internal reference.

Synthesis of $[CuCl(\kappa^1\text{-}S\text{-}L\text{-}NMe)(PPh_3)_2]$ (1): To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in 10 mL of acetonitrile was added PPh_3 (0.132 g, 0.50 mmol). The solution was mildly heated and stirred for a period of 2 h, which led to the formation of white precipitate. The addition of the thio-ligand, L-NMe (0.029 g, 0.25 mmol) made the precipitate to dissolve and a clear solution was obtained. After filtration, about 1 mL of methanol was added and the resulting solution was kept undisturbed for slow evaporation at room temperature (10–15 d). This yielded colorless crystals of **1** (70 %, M.p 155–157 °C).$C_{40}H_{38}ClCuN_2SP_2$: calcd.C 64.89; H 5.14; N 3.79 %; found: C 65.39; H 5.20; N 3.52 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = ν(N–H), 3072 s; ν(C–H), 3013 w, 2888 w; ν(C–C) + ν(C–N) + δ(C–H), 1517 s, 1480 m, 1434s; 1409 w, 1296 m, 1280 m, 1181 w, 1157 w; ν(C–S), 1111 w; ν(P–C_{Ph}), 1092 s; 1027 w, 998 w, 744 s, 694 s, 632 w, 508 s, 489 m cm^{-1}.

Synthesis of $[CuBr(\kappa^1\text{-}S\text{-}L\text{-}NMe)(PPh_3)_2]$ (2): To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in acetonitrile was added PPh_3 (0.091 g, 0.35 mmol). The reaction mixture on stirring and mild heating for a period of 2 h yielded white precipitate. The acetonitrile solvent was removed and the precipitate suspended in chloroform. To the suspension, the thio-ligand L-NMe (0.0202 g, 0.17 mmol) was added and a clear solution obtained was filtered. After filtration 1 mL of methanol was added and the solution was kept undisturbed for crystallization. Slow evaporation of solution at room temperature yielded colorless prismatic crystals of **2** (69 %, M.p. 270–272 °C).$C_{40}H_{38}BrCuN_2P_2S$: calcd.C 61.30; H 4.85; N 3.58 %; found: C 61.40; H 4.61; N 3.70 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = ν(N–H), 3211 s; ν(C–H), 3050 w, 2997 w, 2964 w, 2927 w, 2886 w; ν(C–C) + ν(C–N) + δ(C–H), 1541 s, 1514 s, 1477 m, 1434 s, 1404 w, 1330 m, 1290s, 1179 w, 1154 w; ν(C–S), 1108 s; ν(P–C_{Ph}), 1094s; 1021 w, 998 w, 957 w, 919w, 858 w, 749 s, 698 s, 640 w, 567 w, 520 m, 502 s, 438 w cm^{-1}.

Synthesis of $[Cu_2(\kappa^1\text{-}I)_2(\mu\text{-}S\text{-}L\text{-}NMe)_2(PPh_3)_2]$ (3): To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in 10 mL of acetonitrile, PPh_3 (0.069 g, 0.26 mmol) was added. The solution on stirring and mild heating for 2 h gave precipitate and addition of the thio-ligand L-NMe (0.015g, 0.13 mmol) made a clear solution which was filtered. After filtration, 1 mL of methanol was added and the resulting solution was kept undisturbed for crystallization. The slow evaporation of solution at room temperature (10–15 d) yielded colorless crystals of **3** (65 %, M.p 162–164 °C).$C_{44}H_{46}Cu_2I_2N_4P_2S_2$: calcd.C 46.40; H 4.04; N 4.92 %; found : C 46.20; H 4.10; N 5.20 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = ν(N–H) 3257 m; ν(C–H), 3048 m, 3017 w, 3002 w, 2952 w, 2886 w; ν(C–N)+δ(C–H), 1529 s, 1507 s, 1478 s, 1433 s; 1407 m, 1331 m, 1295 s, 1184 w, 1153w; ν(C = S), 1110 m; ν(P–C_{Ph}), 1092 s; 1026 m, 998 w, 958 w, 918 w, 853 w, 746 s, 638 w, 618 w, 517 s, 501 s cm^{-1}.

Synthesis of $[Cu_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}L\text{-}NEt)_2(PPh_3)_2]$ (4): Procedure (a): To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in acetonitrile was added PPh_3 (0.132 g, 0.50 mmol). The reaction mixture was stirred and mildly heated for 2 h, which yielded white precipitate. The acetonitrile was removed and the precipitate suspended in $CHCl_3$. The addition of thio-ligand L-NEt (0.032 g, 0.25 mmol) made a clear solution which after filtration and addition of 1 mL of methanol was kept undisturbed for crystallization. Slow evaporation of solution at room temperature yielded colorless prismatic crystals. Procedure (b): To a solution of CuCl (0.025 g, 0.25 mmol) in 10 mL of acetonitrile was added solid PPh_3 (0.066 g, 0.25 mmol) followed by stirring for 2 h at room temperature. To the precipitate formed was added L-NEt (0.032 g, 0.25mmol) and finally 1 mL dicholoromethane and the resulting solution was filtered and kept undisturbed for crystallization. Colorless crystals of compound **4** produced within 1 week (70 %, M.p. 260–262 °C). $C_{46}H_{50}Cl_2Cu_2N_4P_2S_2$: calcd.C 56.21; H 5.13; N 5.70 %; found: C 56.10; H 5.08; N 6.24 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = ν(N–H), 3203 s; ν(C–H), 3049 w, 2970 w, 2886 w; ν(C–C) + ν(C–N) + δ(C–H), 1515 s, 1478 s, 1431s; 1380 w, 1360 w, 1321 s, 1282 s, 1261 s, 1221 w, 1191 w; ν(C–S), 1126 w; ν(P–C_{Ph}), 1094 m; 1027 w, 998 w, 943 w, 857 w, 786 w, 752 s, 696 s, 626 m, 609 m, 518 s, 502 s, 434 w cm^{-1}.

Synthesis of $[CuBr(\kappa^1\text{-}S\text{-}L\text{-}NEt)(PPh_3)_2]$ (5): To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in 10 mL of acetonitrile was added PPh_3 (0.092 g, 0.35 mmol). The solution was stirred and mildly heated for 2 h, which formed precipitate and the addition of thio-ligand L-NEt (0.023 g, 0.18 mmol) made a clear solution. After filtration, 1 mL of methanol was added and the resulting solution on slow evaporation of solution at room temperature (10–15 d) yielded colorless crystals of **5** (67 %, M.p 182–184 °C). $C_{41}H_{40}BrCuN_2P_2S$: calcd.C 61.63; H 5.01; N 3.51 %; found : C 61.41; H 5.17; N 3.96 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = ν(N–H), 3196 s; ν(C–H), 3068 m, 3046 m, 3000 w, 2975 m, 2928 w, 2885 w; ν(C–C) + ν(C–N) + δ(C–H), 1512 s, 1479 s, 1433 s, 1356 w, 1377 w, 1321 m, 1280 s, 1264 s, 1180 m, 1155 w; ν(C–S), 1124w; ν(P–C_{Ph}), 1095s; 1073 w, 1028 m, 998 w, 943 w, 913 w, 841 w, 785 w, 748 s, 741 s, 694 s, 627 m, 607 m, 513 s, 505 s, 493 s, 444 w, 431 w cm^{-1}.

Synthesis of $[CuI(\kappa^1\text{-}S\text{-}L\text{-}NEt)(PPh_3)_2]$ (6): To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in 10 mL of acetonitrile was added PPh_3 (0.069 g, 0.26 mmol). The solution was stirred and mildly heated for 2 h and to the precipitate thio-ligand L-NEt (0.017g, 0.13 mmol) was added. A clear solution obtained was filtered, 1 mL of methanol was added and slow evaporation of solution at room temperature (10–15 d) yielded colorless crystals of **6** (65 %, M.p. 179–181°C). $C_{41}H_{38}CuIN_2P_2S$: calcd. C 58.34; H 4.51; N 3.32 %; found: C 58.10; H 4.65; N 3.44 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = : ν(N–H) 3261 m; ν(C–H) 3048 m, 2974 w, 2961 w, 2928 w, 2884 w; ν(C–C) + ν(C–N) + δ(C–H), 1518 s, 1506 s, 1478 s, 1433 s, 1379 w, 1357 w, 1320 m, 1282 s, 1256 s, 1153 w; ν(C–S), 1125 m; ν(P–C_{Ph}) 1092 s; 1072 m, 1026 m, 997 m, 945 w, 857 w, 791 w, 746 s, 696 s, 624 m, 517 s, 502 s cm^{-1}.

Synthesis $[CuCl(\kappa^1\text{-}S\text{-}L\text{-}NPh)(PPh_3)_2]$ (7): Procedure (a): To a solution of copper(I) chloride (0.025 g, 0.25 mmol) in 10 mL of acetonitrile was added PPh_3 (0.132 g, 0.50 mmol). The solution was stirred and mildly heated for 2 h which yielded white precipitate and after removal of acetonitrile solvent, 5 mL $CHCl_3$ was added. To this suspension was added thio-ligand L-NPh (0.045 g, 0.25 mmol). A clear solution obtained was filtered and 1 mL of methanol was added to the solution. Slow evaporation of solution at room temperature (10–15 d) yielded colorless crystals. Procedure (b): To a solution of CuCl (0.025 g, 0.25 mmol) in 10 mL of acetonitrile was added solid PPh_3

(0.066 g, 0.25 mmol) followed by stirring for 2 h at room temperature. To the precipitate formed was added L-NPh (0.045 g, 0.25 mmol) and finally 1 mL dicholoromethane and the resulting solution was filtered and kept undisturbed for crystallization. Colorless crystals of **7** (68 %, M.p 174–184°C) were produced within one week. $C_{45}H_{40}ClCuN_2P_2S$: calcd.C 67.35; H 4.99; N 3.49 %; found: C 67.15; H 5.03; N 3.62 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = ν(N–H) 3184 s; ν(C–H) 3051 s, 3001 w, 2955 w, 2894 w; ν(C–N)+δ(C–H) 1584 m, 1596 m, 1511 s, 1499 s, 1453 w, 1434 s, 1340 w, 1305 m, 1288 m, 1267 m, 1248 s, 1199 w, 1185 w, 1157 w; ν(C–S), 1120 w; ν(P–C_{Ph}), 1093 s; 1071 w, 1041 w, 1028 m, 999 m, 949 m, 900 w, 848 w, 757 s, 746 s, 694 s, 665 m, 635 w, 618 w, 551 s, 518 s, 503 s, 422 w, 442 w cm^{-1}.

Synthesis of [CuBr(κ^1-S-L-NPh)(PPh$_3$)$_2$] (8): To a solution of copper(I) bromide (0.025 g, 0.17 mmol) in 10 mL of acetonitrile was added PPh_3 (0.092 g, 0.35 mmol). The solution was stirred and mildly heated for 2 h and to the precipitate thio-ligand L-NPh (0.031 g, 0.17 mmol) was added. A clear solution obtained was filtered and 1 mL of methanol was added. Slow evaporation of solution at room temperature (10–15 d) yielded colorless crystals of **8** (62 %, M.p 175–177 °C). $C_{45}H_{40}BrCuN_2P_2S$: calcd. C 63.81; H 4.73; N 3.31 %; found: C 63.50; H 4.50; N 3.10 %. **IR** (KBr, absorption bands): $\tilde{\nu}$ = ν(N–H) 3117 s; ν(C–H) 3050 s, 3002 w, 2957 w, 2895 w, 1596 m, 1584 m, 1498 s, 1478 s, 1453 w, 1433 s, 1339 w, 1328 w, 1298 m, 1287 m, 1251 s, 1184 w; ν(C–S), 1157 w; ν(P–C_{Ph}) 1092 s; 1071 w, 1026 m, 1038 w, 998 m, 972 w, 947 w, 899 w, 849 w, 824 w, 746 s, 693 s, 634 w, 618 w, 550 s, 518 s, 502 s, 442 w, 421 w cm^{-1}.

X-ray Crystallography: The single crystals of compounds were mounted on glass fibers and data were collected with an Xcalibur, Eos, Gemini (**1**, **4**, **7**, **8**) and a Bruker APEX-II CCD (**2**, **3**, **5**, **6**) diffractometer, equipped with a graphite monochromator and Mo-K_α radiation (λ = 0.71073 Å; **2**–**8**,) and Cu-K_α radiation (λ = 1.54178 Å; **1**). The unit cell dimensions and intensity data were measured at 173(2) K (for **1**, **4**, **7**, **8**) and 296(2) K (for **2**, **3**, **5**, **6**). The data collection, cell refinement were processed with CrysAlisPro and data reduction processed with CrysAlisRED (**1**, **4**, **7**, **8**).[42] The data for other compounds (**2**, **3**, **5**, **6**) collected with Bruker APEX2, while cell refinement and data reduction carried out with Bruker SAINT (cell refinement, data reduction, data collection).[43] The structures were solved by direct methods using the program SHELXS97, SIR-92[44,45] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97[46]

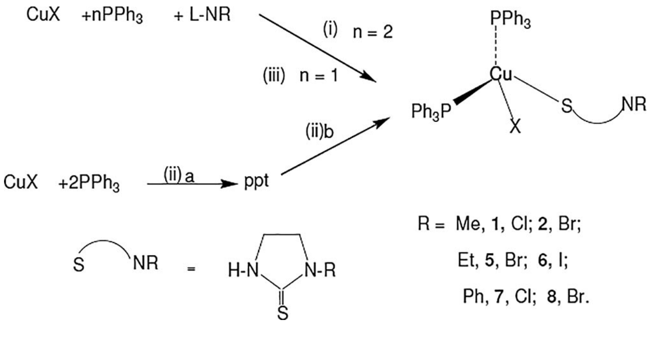
Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1054767 (**1**), CCDC-1054547 (**2**), CCDC-1054550 (**3**), CCDC-1054551 (**4**), CCDC-1054548 (**5**), CCDC-1054549 (**6**), CCDC-1054552 (**7**), and CCDC-1054553 (**8**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Supporting Information (see footnote on the first page of this article): More details about ligands and X-ray packing figures.

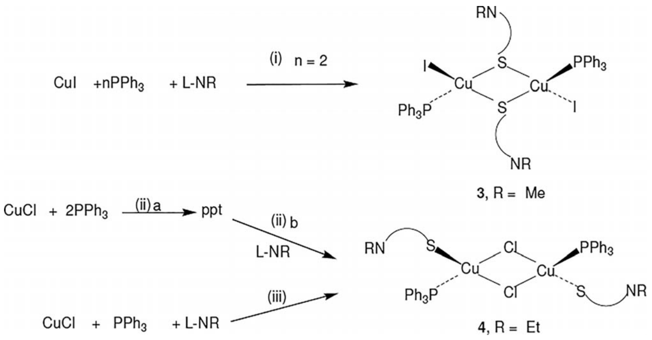
Results and Discussion

Synthesis and IR spectroscopy

The imidazolidine-2-thione based thio-ligands, L-NMe, L-NEt and L-NPh, were reacted with copper(I) halides (X = Cl, Br, I) and triphenylphosphine (PPh_3) in acetonitrile for preparing the mixed ligand complexes (molar ratio used: Cu:PPh_3:thio-ligand 1:2:1). Scheme 2 shows the formation of mono-nuclear complexes (**1**, **2**, **5**–**8**) and Scheme 3 that of di-nuclear complexes (**3**, **4**). The preferred order of reaction used is initially reacting a copper(I) halide with PPh_3 followed by the addition of a thio-ligand in situ [Scheme 2, route (i) for **1**, **5**, **6**, **8**; Scheme 3 , route (i) for **3**]. In case the mixed ligand complex is not obtained, acetonitrile is removed after initially binding a copper(I) halide with PPh_3 and then the precipitate is suspended in chloroform followed by the reaction with a thio-ligand [Scheme 2, route (ii) for **2**, **7**]. The addition of small amount of methanol/dichloroform helped in crystallization. The chloro bridged dinuclear complex **4** was obtained by using 1:2:1 molar ratio (Cu:PPh_3:thio-ligand) through route (ii) and using 1:1:1 molar ratio through route (iii) (see Scheme 3). It was found that reaction of copper(I) chloride with PPh_3 and L-NPh in 1:1:1 molar ratio in CH_3CN/CH_2Cl_2 [route (iii)] also gave the same mononuclear complex **7** as obtained by route (ii) (Scheme 2).



Scheme 2. Synthesis of complexes (i) CH_3CN/MeOH (**1**, **5**, **6**, **8**), (ii) (a) CH_3CN, (b) $CHCl_3$/MeOH (**2**, **7**), and (iii) CH_3CN/CH_2Cl_2 (**7**).



Scheme 3. Synthesis of dinuclear complexes: (i) CH_3CN/MeOH (**3**), (ii) (a) CH_3CN, (b) $CHCl_3$/MeOH, and (iii) CH_3CN/CH_2Cl_2 (**4**).

All complexes have shown the ν(N–H) bands in the region 3070–3265 cm^{-1} which are medium to strong in intensity and reveal that the thio ligands are binding to central metal atoms as neutral ligands. These bands either move to low energy region (**1**, **7**, **8**) or to high energy region (**2**–**6**) relative to the uncoordinated thio ligands [ν(N–H), 3196 m, L-NMe; 3188 m, L-NEt; 3203 s, L-NPh]. Likewise the ν(C–S) bands in the free ligands occur in the region 1178 to 1200 cm^{-1} [ν(C–S), 1200 s, L-NMe; 1199 s, L-NEt; 1178 m, L-NPh], which shift to low energy region (1100–1160 cm^{-1}) in complexes which support that the thio ligands are coordinating through its thione sulfur to central metal atoms as neutral ligand. The ν(P–C_{Ph}) bands in the region 1090 to 1100 cm^{-1} showed the presence of coordinated PPh_3 in complexes. The above IR data support coordination of thio ligands and PPh_3 as neutral ligands through sulfur and phosphorus respectively (see Experimental Section and Supporting Information for more IR details).

Crystal and Molecular Structures

Complexes **2**–**4**, **7**, and **8** each formed crystals in the triclinic system with $P\bar{1}$ space group, the other complexes **1**, **5** and **6** each crystallized in monoclinic crystal system with space groups $P2_1/c$, $C2/c$, and $P2_1/n$ respectively (Table 1). Most of complexes fall in two categories: four coordinated mononuclear (**1**, **2**, **5**–**8**) and dinuclear (**3** and **4**). The geometric parameters are briefly discussed below.

Mononuclear Complexes

In complex [CuCl(κ^1-S-L-NMe)(PPh_3)$_2$] (**1**), the thio-ligand L-NMe is bonded to the central copper(I) metal through its sulfur donor atom at Cu–S bond length of 2.4154(6) Å. Copper(I) is also bonded to P donor atoms of two PPh_3 ligands at Cu–P distances of 2.2865(5) and 2.2967(5) Å, and to one chloride anion at Cu–Cl distance of 2.3440(5) Å (Table 2). The bond angles lie in the range of 98.92(2) to 121.92(2)°, which

Table 1. Crystallographic data for complexes **1**–**8**.

	1	2	3	4
Empirical formula	$C_{40}H_{38}ClCuN_2P_2S$	$C_{40}H_{38}BrCuN_2P_2S{\cdot}C_{36}H_{30}BrCuP_2$	$C_{44}H_{46}Cu_2I_2N_4P_2S_2$	$C_{46}H_{50}Cl_2Cu_2N_4P_2S_2$
M	739.72	1452.17	1137.83	982.94
T /K	173(2)	296(2)	296(2)	173(2)
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	14.3620(5)	9.8946(6)	9.609(3)	9.1060(6)
b /Å	10.1350(3)	17.6174(11)	9.824(3)	10.1794(9)
c /Å	24.5148(9)	19.9244(13)	13.756(5)	13.4004(10)
α /°	90	84.274(3)	102.644(16)	79.020(7)
β /°	91.901(3)	88.539(4)	90.783(17)	73.800(7)
γ /°	90	79.225(3)	116.723(14)	70.193(7)
V /Å^3	3566.4(2)	3394.8(4)	1122.3(7)	1115.90(16)
Z	4	2	1	1
$D_{calcd.}$ /g·cm^{-3}	1.378	1.421	1.683	1.463
μ /mm^{-1}	3.186	1.973	2.523	1.267
F(000)	1536	1484	564	508
Reflections collected	23241	64016	21651	12365
Unique reflections	6907 (R_{int}, 0.0429)	17307 (R_{int}, 0.0444)	6171 (R_{int}, 0.0335)	7273 (R_{int}, 0.0338)
Data/ restraints / parameters	6907 / 0 / 430	17307/ 0 / 784	6171/ 0 / 257	7273/ 0 / 263
Reflections with [$I > 2\sigma(I)$]	6151	10623	5347	6094
R (reflections)	0.0362 (6151)	0.0401(10623)	0.0270 (5347)	0.0374(6094)
WR2 (reflections)	0.0968(6907)	0.0894(17307)	0.0685(6171)	0.0968 (7273)
Largest diff. peak and hole /e·Å^{-3}	0.484 and –0.343	0.543 and –0.755	0.511 and –0.788	0.452 and –0.447

	5	6	7	8
Empirical formula	$C_{41}H_{40}BrCuN_2P_2S$	$C_{41}H_{38}CuIN_2P_2S$	$C_{45}H_{40}ClCuN_2P_2S$	$C_{45}H_{40}BrCuN_2P_2S$
M	798.21	843.19	801.80	846.24
T /K	296(2)	296(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a /Å	35.917(3)	12.9335(9)	10.2292(5)	10.3251(5)
b /Å	12.8242(10)	21.4828(11)	12.8630(7)	12.8502(6)
c /Å	17.6358(13)	14.5224(9)	15.3861(8)	15.4540(7)
α /°	90	90	75.944(4)	76.242(4)
β /°	113.559(4)	104.301(2)	79.403(4)	79.258(4)
γ /°	90	90	79.235(4)	79.566(4)
V /Å^3	7446.1(10)	3910.0(4)	1908.79(17)	1936.52(16)
Z	8	4	2	2
$D_{calcd.}$ /g·cm^{-3}	1.424	1.432	1.395	1.451
μ /mm^{-1}	1.834	1.514	0.816	1.767
F(000)	3280	1704	832	868
Reflections collected	53991	40770	25980	25461
Unique reflections	13386 (R_{int}, 0.0611)	10150 (R_{int}, 0.0465)	12653 (R_{int}, 0.0362)	12864 (R_{int}, 0.0391)
Data/ restraints / parameters	13386/ 0 / 433	10150/ 0 / 434	12653 / 0 / 470	12864/ 0 / 470
Reflns.with [$I > 2\sigma(I)$]	7783	6344	10191	9596
R (reflections)	0.0407(7783)	0.0408(6344)	0.0389(10191)	0.0422(9596)
wR_2 (reflections)	0.0999 (13386)	0.0982(10150)	0.0996(12653)	0.0868(12864)
Largest diff. peak and hole /e·Å^{-3}	0.337 and –0.560	0.597 and –0.416	0.617 and –0.490	0.512 and –0.503

suggest distorted tetrahedral arrangement of complex **1** (Figure 1). The bonding pattern of other mononuclear complexes is similar except that there is difference in anions (Br, **2**, **5**, **8**; I, **6**, Cl, **7**) and thio ligands, which alter bond lengths and angles around the central metal atoms (Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6). The P–Cu–P bond angles of the mononuclear complexes lie in the usual range, ca. 121–126°.[29–38]

Complex [(CuBr(κ^1-S-L-NMe)(PPh$_3$)$_2$.CuBr(PPh$_3$)$_2$] (**2**) has two different four and three coordinated independent molecules in the unit cell. The latter moiety CuBr(PPh$_3$)$_2$ has two PPh$_3$ ligands and a bromide bonded to a central metal

Table 2. Bond parameters /Å,° of complexes **1**–**8**.

[CuCl(κ^1-S-L-NMe)(PPh$_3$)$_2$] (**1**)		[CuBr(κ^1-S-L-NMe)(PPh$_3$)$_2$] (**2**)	
Cu1–Cl1	2.3440(5)	Cu1–Br1[a)]; Cu2–Br2[b)]	2.4821(4)[a)]; 2.3331(4)[b)]
Cu1–S1	2.4154(6)	Cu1–S1[a)]	2.3976(7)[a)]
Cu1–P1	2.2865(5)	Cu1–P1[a)]; Cu2–P3[b)]	2.2718(7)[a)]; 2.2626(7)[b)]
Cu1–P2	2.2967(5)	Cu1–P2[a)]; Cu2–P4[b)]	2.2877(7)[a)]; 2.2638(7)[b)]
S1–C37	1.697(2)	S1–C37[a)]	1.687(3)[a)]
Cl1–Cu1–S1	108.759(19)	Br1–Cu1–S1[a)]	110.05(2)[a)]
P1–Cu1–S1	103.99(2)	P1–Cu1–S1[a)]	109.50(3)[a)]
P2–Cu1–S1	112.92(2)	P2–Cu1–S1[a)]	98.66(3)[a)]
P1–Cu1–Cl1	110.76(2)	P1–Cu1–Br1[a)]; P3–Cu2–Br2[b)]	102.46(2)[a)]; 115.73(2)[b)]
P1–Cu1–P2	121.17(2)	P1–Cu1–P2[a)]; P3–Cu2–P4[b)]	125.26(3)[a)]; 128.98(3)[b)]
P2–Cu1–Cl1	98.92(2)	P2–Cu1–Br1[a)]; P4–Cu2–Br2[b)]	110.61(2)[a)]; 115.26(2)[b)]
Cu1–S1–C37	110.52(7)	Cu1–S1–C37[a)]	109.81(9)[a)]
[Cu$_2$I$_2$(μ-S-L-NMe)$_2$(PPh$_3$)$_2$] (**3**)		[Cu$_2$(μ-Cl)$_2$(κ^1-S-L-NEt)$_2$(PPh$_3$)$_2$] (**4**)	
Cu1–I1	2.5743(10)	Cu1–Cl1	2.3913(5)
Cu1–S1	2.3935(9)	Cu1–Cl1	2.5060(5)
Cu1–S1	2.4789(8)	Cu1–S1	2.3127(5)
Cu1–P1	2.2489(10)	Cu1–P1	2.2380(5)
S1–C19	1.711(2)	S1–C19	1.7079(17)
Cu1–S1–Cu1	92.07(3)	Cu1–Cl1–Cu1	84.312(16)
S1–Cu1–S1	87.93(3)	Cl1–Cu1–Cl1	95.687(16)
I1–Cu1–S1	115.32(2)	Cl1–Cu1–S1	114.451(17)
I1–Cu1–S1	105.45(3)	Cl1–Cu1–S1	105.460(17)
P1–Cu1–S1	108.32(3)	P1–Cu1–S1	114.738(18)
P1–Cu1–S1	120.04(3)	P1–Cu1–Cl1	109.786(17)
P1–Cu1–I1	116.67(3)	P1–Cu1–Cl1	114.453(17)
Cu1–S1–C19	113.32(7)	Cu1–S1–C19	110.20(6)
[CuBr(κ^1-S-L-NEt)(PPh$_3$)$_2$] (**5**)		[CuI(κ^1-S-L-NEt)(PPh$_3$)$_2$] (**6**)	
Cu1–Br1	2.4845(4)	Cu1–I1	2.6733(4)
Cu1–S1	2.3868(6)	Cu1–S1	2.3785(9)
Cu1–P1	2.2966(6)	Cu1–P1	2.2958(8)
Cu1–P2	2.2750(6)	Cu1–P2	2.2864(8)
S1–C37	1.701(2)	S1–C37	2.2864(8)
S1–Cu1–Br1	111.199(18)	S1–Cu1–I1	112.44(2)
P1–Cu1–S1	101.98(2)	P1–Cu1–S1	102.99(3)
P2–Cu1–S1	103.93(2	P2–Cu1–S1	108.95(3)
P1–Cu1- Br1	105.367(17)	P1–Cu1–I1	105.45(2)
P2–Cu1–Br1	107.825(16)	P2–Cu1–I1	103.20(2)
P2–Cu1–P1	126.14(2)	P2–Cu1–P1	123.91(3)
C37–S1–Cu1	110.00(7)	C37–S1–Cu1	110.21(11)
[CuCl(κ^1-S-L-NPh)(PPh$_3$)$_2$] (**7**)		[CuBr(κ^1-S-L-NPh)(PPh$_3$)$_2$] (**8**)	
Cu1–Cl1	2.3297(4)	Cu1–Br1	2.4510(3)
Cu1–S1	2.4448(5)	Cu1–S1	2.4342(5)
Cu1–P1	2.2626(4)	S1–C1	1.692(2)
Cu1–P2	2.2824(4)	Cu1–P1	2.2634(5)
S1–C1	1.6944(16)	Cu1–P2	2.2802(5)
Cl1–Cu1–S1	103.874(16)	S1–Cu1–Br1	105.373(16)
P1–Cu1–S1	102.955(16)	P1–Cu1–S1	103.60(2)
P2–Cu1–S1	106.218(16)	P2–Cu1–S1	106.951(19)
P1–Cu1–Cl1	108.102(16)	P1–Cu1–Br1	105.518(16)
P2–Cu1–Cl1	108.964(17)	P2–Cu1–Br1	108.427(17)
P1–Cu1–P2	124.703(16)	P1–Cu1–P2	125.381(19)
C1–S1–Cu1	101.87(6)	C1–S1–Cu1	102.94(7)

a) Refers to parameters of molecule 1. b) Refers to parameters of molecule 2.

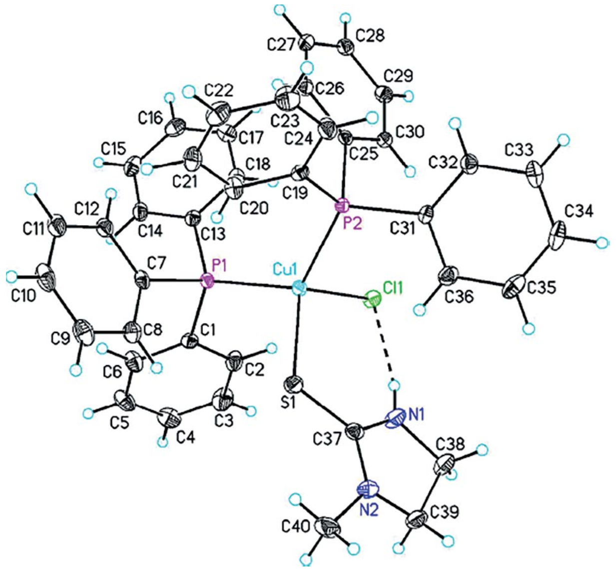


Figure 1. Molecular structure of [CuCl(κ^1-S-L-NMe)(PPh_3)$_2$] (**1**).

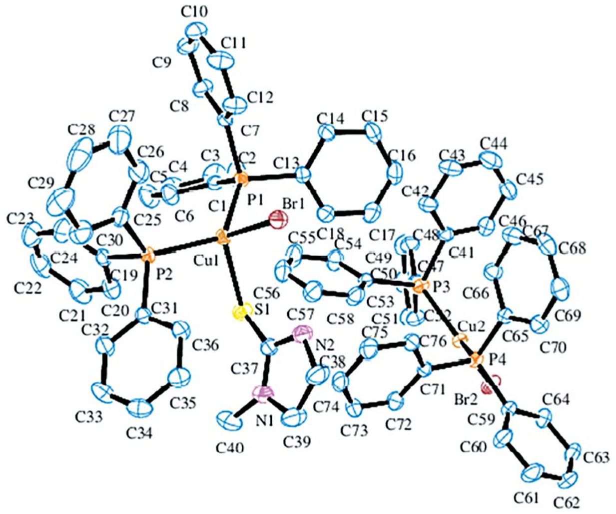


Figure 2. Molecular structure of [(CuBr(κ^1-S-L-NMe)(PPh_3)$_2$). CuBr(PPh_3)$_2$] (**2**).

atom and angles around the metal atom (115–129°) suggest a distorted trigonal planar arrangement. A related thio ligand, 1,3-imidazoline-2-thione (L′-NH) is reported to yield mononuclear copper(I) complexes, [Cu*X*(L′-NH)(PPh_3)$_2$] (*X* = Br, I) similar to monomer **1** as well as a mixed coordinate complex [(CuCl(κ^1-S-L′-NH)(PPh_3)$_2$.CuCl(PPh_3)$_2$] similar to complex **2**.[47] The bond parameters of complexes under study are similar to those reported for L′-NH ligand[47]and other heterocyclic-2-thiones.[29–38]

Dinuclear Complexes

Complex [Cu_2I_2(μ-S-L-NMe)$_2$(PPh_3)$_2$] (**3**) has each copper(I) ion bonded to two bridging S, one P and one I donor species at Cu–S, Cu–P and Cu–I bond lengths of 2.3935(9), 2.4789(8); 2.2489(10) and 2.5743(10) Å, respectively (Figure 7).[48,49] The unequal Cu–S distances, 2.3935(9), 2.4789(8) Å suggest that Cu_2S_2 core forms a parallelogram. The angles around the central copper atoms vary in the range of ca. 88 to 120° suggesting distorted tetrahedral arrangement of each central metal atom. The angles of Cu_2S_2core, namely, Cu–S–Cu, 92.07(3)° and S–Cu–S, 87.93(3)° are much different from usually observed ideal values of ca. Cu–S–Cu, 70° and S–Cu–S 109° shown by parallelograms of such Cu_2S_2 cores.[48,49]

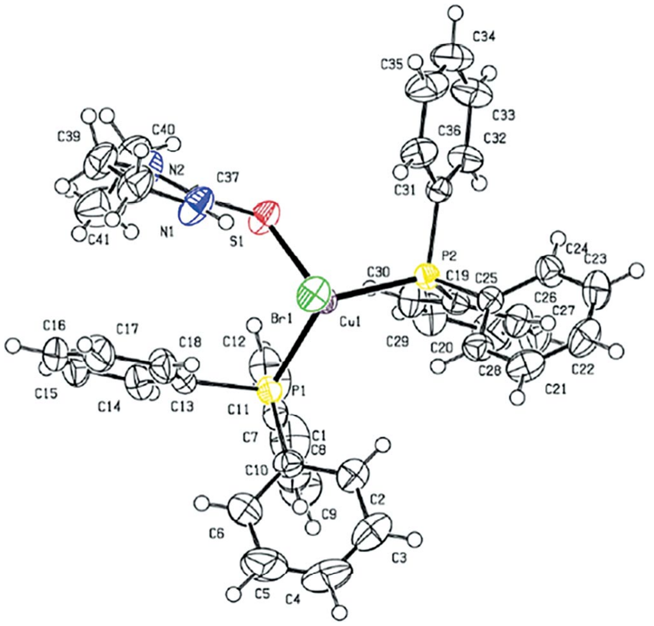


Figure 3. Molecular structure of [CuBr(κ1-S-L-NEt)(PPh3)2] (**5**).

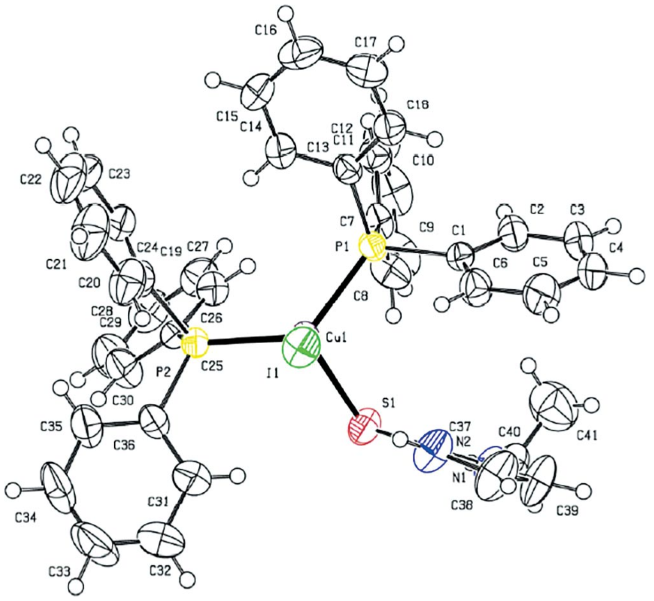


Figure 4. Molecular structure of [CuI(κ^1-S-L-NEt)(PPh_3)$_2$] (**6**).

The second dimer [Cu_2(μ-Cl)$_2$(κ^1-S-L-NEt)$_2$(PPh_3)$_2$] (**4**) has each copper metal atom bonded to two bridging Cl, one P and one S atoms at bond lengths of 2.3913(5), 2.5060(5); 2.2380(5)

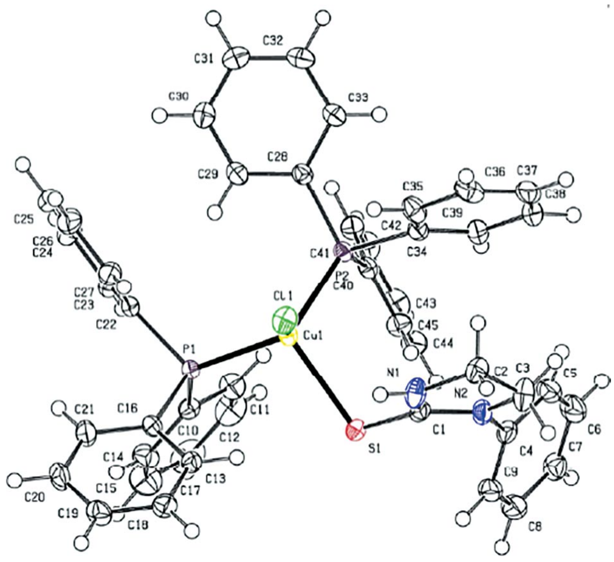


Figure 5. Molecular structure of [CuCl(κ^1-S-L-NPh)(PPh_3)$_2$] (**7**).

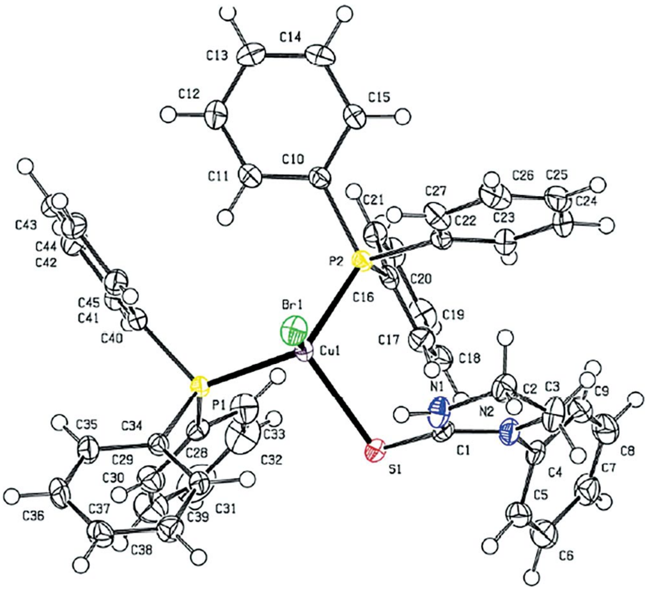


Figure 6. Molecular structure of [CuBr(κ^1-S-L-NPh)(PPh_3)$_2$] (**8**).

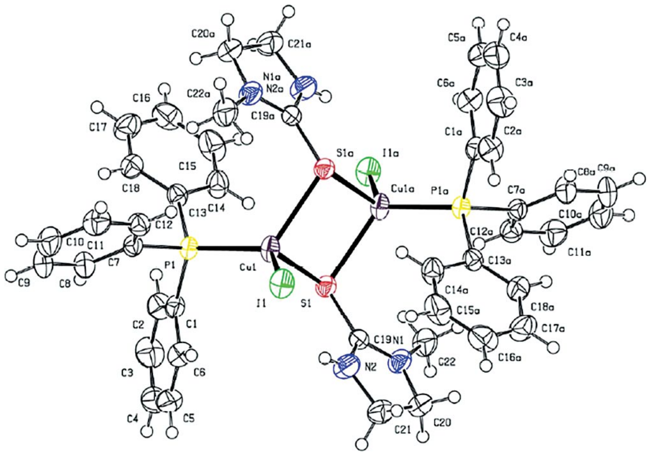


Figure 7. Molecular structure of [Cu_2I_2(μ-S-L-NMe)$_2$(PPh_3)$_2$] (**3**).

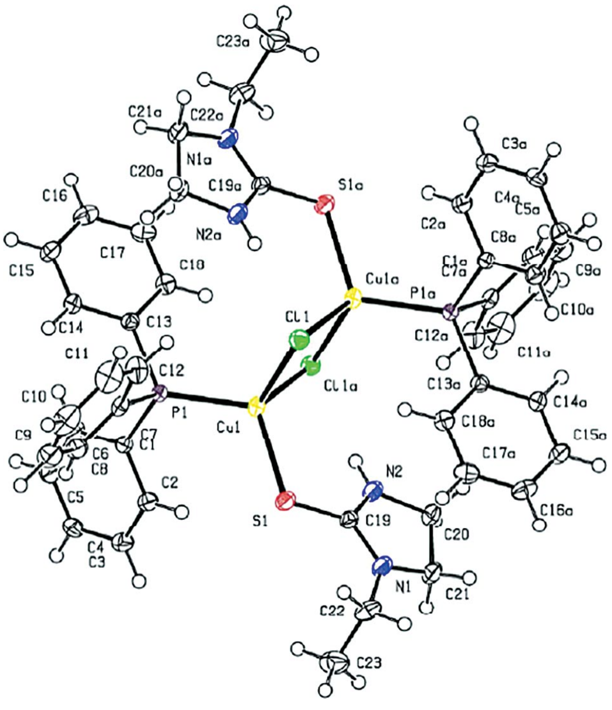


Figure 8. Molecular structure of [Cu_2(μ-Cl)$_2$(κ^1-S-L-NEt)$_2$(PPh_3)$_2$] (**4**).

and 2.3127(5) Å, respectively (Figure 8). The Cu–S distance is short as thio ligand L-NEt is terminally bonded unlike μ-S bridging by L-NMe in **3**. The angles around the central copper atoms vary in the range of ca. 95 to 115° suggesting distorted tetrahedral arrantgement of each central metal atom. It is known that the C–S double bond length is 1.62°A, whereas the C–S single bond length is 1.81 Å.[50,51] A comparison of C–S bond lengths observed in different complexes (Table 2) reveals a variation from 1.687 to 1.711 Å, which suggests a considerable double bond character in this bond. Complex **3** shows the longest C–S bond due to Cu–S–Cu bridging occurring in this complex.

It was observed recently by our group that the ligands under discussion formed dinuclear complexes with silver(I) chloride/bromide and each thio ligand was terminal and only halogen atoms were bridging two silver atoms. In this context complex **4** (*X* = Cl) shows the same halogen bridging behavior.[52] However, this trend appears to be reversed in complex **3** (*X* = I) due to the presence of bulky iodide, which has favored terminal bonding.

Proton NMR Spectroscopy

Table 3 gives ^{1}H NMR spectroscopic data of complexes **1**–**8**. The most sensitive protons of thio ligands to coordination are –NH protons, while ring protons are generally less affected except in complex **2**. Thus complexes **1**, **2**, **4**–**8** showed NH signals in the region 7.72 to 9.87 ppm, significantly to low field relative to the uncoordinated ligands (6.09 to 6.53 ppm),

Table 3. ^{1}H NMR spectroscopic data (δ in ppm) of complexes **1**–**8**.[a)]

Compound	Ring + N–R protons	PPh$_3$	Compound	Ring + N–R protons	PPh$_3$
1	8.64 s (NH) 3.65 m (C^{4}H$_2$), 3.59 m (C^{5}H$_2$), 3.07 s (CH$_3$)	7.44 m (12 H, *o*-H), 7.36 m (6 H, *p*-H), 7.30 m (12 H, *m*-H)	**5**	8.36 s (NH) 3.61 m (C^{4}H$_2$), 3.55 m (C^{5}H$_2$,N-CH$_2$), 1.41 t (CH$_3$)	7.44 m (12 H, *o*-H), 7.36 m (6 H, *p*-H), 7.28 m (12 H, *m*-H)
2	8.55 s (NH) 3.68 m (C^{4}H$_2$), 3.57 m (C^{5}H$_2$), 3.01 m (CH$_3$)	7.39 m (12 H, *o*-H), 7.35 m (6 H, *p*-H), 7.30 m (12 H, *m*-H)	**6**	7.72 s (NH) 3.62 m (C^{4}H$_2$), 3.55 m (C^{5}H$_2$, N-CH$_2$), 1.15 t (CH$_3$)	7.44 m (12 H, *o*-H), 7.36 m (6 H, *p*-H), 7.28 m (12 H, *m*-H)
3	6.03 s (NH) 2.04 m (C^{4}H$_2$), 1.94 m (C^{5}H$_2$), 1.45 s (CH$_3$)	5.85 m (12 H, *o*-H), 5.77 m (6 H, *p*-H), 5.69 m (12 H, *m*-H)	**7**	9.87 s (NH) 4.08 t (C^{4}H$_2$), 3.76 t (C^{5}H$_2$), 7.40 m (*p*-H, N–Ph)	7.44 m (14 H, *o*-H),[b)] 7.36 m (6 H, *p*-H), 7.28 m (14 H, *m*-H)[b)]
4	9.31 s (NH) 3.72 bs (C^{4,5}H$_2$), 3.60 q (N–CH$_2$), 1.21t (CH$_3$)	7.51 m (12 H, *o*-H), 7.40 m (18 H, *m*-H and, *p*-H)	**8**	9.13 s (NH) 4.01 t (C^{4}H$_2$), 3.65 t (C^{5}H$_2$)	7.43 m (14 H, *o*-H),[b)] 7.36 m (7 H, *p*-H),[b)] 7.26 m (14 H, *m*-H)[b)]
L-NMe	6.09s (NH), 3.72 m (C^{4}H$_2$), 3.58m (C^{5}H$_2$), 3.15 s (CH$_3$)				
L-Net	6.09 s(NH),3.68 m (C^{4}H$_2$, N-CH$_2$), 3.58 m (C^{5}H$_2$), 1.20 t (CH$_3$)				
L-NPh	6.53s (NH), 4.19m (C^{4}H$_2$), 3.76m (C^{5}H$_2$), 7.59m (*o*-H, N–Ph),7.43 m (*m*-H, N–Ph), 7.27 m (*p*-H, N–Ph)				

a) Proton NMR spectra of **1**, **3**–**8** recorded in CDCl$_3$ and that of **2** in CDCl$_3$ + D$_6$[DMSO]. b) Incorporate N–Ph hydrogen signals.

Table 4. Intramolecular N/H···halogen contacts /Å.

Compound	*X*	*d*(*X*–H)	*d*(H–*X*), van der Waals	Δ*d*$_1$	*d*(N–*X*)	*d*(N–X), van der Waals	*d*(N–X)	Δ*d*$_2$
1	Cl	2.291	2.9	0.609	3.097	3.25	3.097	0.153
2	Br	2.711	3.0	0.289	3.362	3.35	3.362	–0.012
3	I	2.913	3.15	0.237	3.608	3.5	3.608	–0.108
4	Cl	2.403	2.9	0.497	3.222	3.25	3.222	0.028
5	Br	2.509	3.0	0.491	3.336	3.35	3.336	0.014
6	I	2.848	3.15	0.302	3.635	3.5	3.635	–0.135
7	Cl	2.528	2.9	0.372	3.145	3.25	3.145	0.105
8	Br	2.677	3.0	0.323	3.294	3.35	3.294	0.056

except complex **2**, in which this signal is unaffected as well as its ring proton signals (C^{4}H$_2$, C^{5}H$_2$, N-Me) moved to high field. Further, it can be seen that for –NH signas, the magnitude of shift varies in the order : Cl > Br > I. It is added here that X-ray crystallography has shown that there is an intramolecular interaction involving the N–H···*X*(halogen) moiety. From Table 4 it can be seen that *d*(H···*X*) and *d*(N···*X*) distances are less than the sum of van der Waals radii of atoms participating in these bonds for *X* = Cl and Br and are more for *X* = I. These interactions decrease with the decrease of electronegativity of a halogen. The ring protons (C^{4,5}H$_2$) appeared as triplets in **7** and **8**, while these are multiplets in other complexes (**1**–**6**), due to lack of resolution/interference of N–Me and N–Et protons. The *o*-, *m*- and *p*-hydrogen atoms of PPh$_3$ show signals in separate regions, and also incorporate N–Ph signals of the L-NPh ligand coordinated to central metal atoms for complexes **7** and **8**.

Conclusions

A series of mixed ligand mono- and dinuclear complexes of copper(I) halides with imidazolidine-2-thiones and PPh$_3$ (as co-ligand) **1**–**8** are synthesized, which represent first examples of this class of thio ligands. Three types of complexes are formed: mononuclear tetrahedral [CuX(L-NR)(PPh$_3$)$_2$], halogen- and sulfur-bridged dimers, [Cu$_2$(μ-Cl)$_2$(κ^1-S-L-NEt)$_2$(PPh$_3$)$_2$] and [Cu$_2$I$_2$(μ-S-L-NMe)$_2$(PPh$_3$)$_2$]. In silver(I) halide (chloride/bromide) complexes of this class of thio ligands with PPh$_3$ as a co-ligand, it was found that halogen bridging was favored over sulfur bridging,[52] and this trend continues with copper(I) chloride, though with copper(I) iodide, the trend is reversed. It is added here that pyridine-2-thione has displayed essentially sulfur-bridging in its dinuclear complexes.[49] Reaction of copper(I) chloride/bromide with thio ligands under discussion in the absence of PPh$_3$ involved C–S rupture forming copper(II) sulfate, but other products could not be identified. The binding of copper(I) chloride/bromide to PPh$_3$ followed by binding to sulfur of thio ligands has yielded stable mixed-ligand copper(I) complexes.

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