# Interaction of Benzo-1,3-thiazoline-2-thione and Related Ligands with Copper(II) Salts and the Single-crystal *X*-Ray Structure of μ-[1,2-Bis-(diphenylphosphino)ethane]-bis{(benzo-1,3-thiazole-2-thiolato-*S*)[1,2-bis(diphenylphosphinoethane]copper(I)}†

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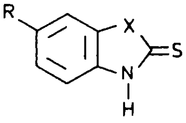
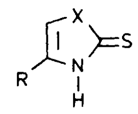
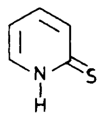
A reinvestigation of the reaction of benzo-1,3-thiazoline-2-thione ($HL^1$) with copper(II) salts has shown, in contradiction to earlier reports, that only two compounds are formed, *viz.* $[Cu(L^1)]$ from aqueous ethanol and $[Cu(HL^1)_2Cl]$ from absolute ethanol. The incorrect formulations arise from contamination of the copper(I) complexes with bis(benzo-1,3-thiazol-2-yl) disulphide ($L^1$–$L^1$). These findings are supported by the reaction of other heterocyclic thioamides and diphenyldithiophosphinic acid with copper(II) salts. The complex $[Cu(L^1)]$ reacts with the chelating phosphines 1,2-bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe), to give $[Cu(L^1)(dppm)]$ and $[Cu_2(L^1)_2(dppe)_3]$. The crystal and molecular structure of $[Cu_2(L^1)_2(dppe)_3]$ has been determined by *X*-ray diffraction techniques. The crystals of the complex are triclinic, space group $P\bar{1}$, with $a = 17.334(3)$, $b = 17.348(2)$, $c = 20.110(2)$ Å, $\alpha = 82.54(1)$, $\beta = 120.73(1)$, $\gamma = 123.86(1)°$, and $Z = 2$. After full-matrix least-squares refinement the final $R$ value was 0.096 for 3 317 reflections. The complex consists of a centrosymmetric dppe-bridged dimer. Each copper atom has a distorted tetrahedral geometry with one phosphorus from the bridging dppe, two phosphorus atoms from a chelating dppe, and the exocyclic sulphur atom from the anionic $L^1$ ligand making up the co-ordination sphere.

The co-ordination chemistry of benzo-1,3-thiazoline-2-thione ($HL^1$), commonly known as 2-mercaptobenzothiazole, and related heterocyclic thione donors has been stimulated by their wide ranging applications.[1] For instance $HL^1$ and its derivatives are used in the rubber vulcanisation process as accelerators.[2] An important step in this process is the formation of reactive intermediates of the accelerator with zinc(II) and progress has been made towards defining the nature of this interaction in $HL^1$ zinc compounds.[3] The compound $HL^1$ has also proved suitable as a corrosion inhibitor for copper[4] although its chemistry with this metal is less well understood. Recently a crystalline compound was isolated by Raper *et al.*[5] from the reaction of copper(II) perchlorate and $HL^1$ in aqueous ethanol and shown to contain tetranuclear cluster cations $[Cu_4(HL^1)_{10}]^{4+}$. Normally ill defined amorphous precipitates are obtained, for which a number of contradictory formulations have been proposed, *viz.* copper(I) complexes $[Cu(L^1)]$,[6,7] $[Cu(L^1)(HL^1)]$,[6] $[Cu(L^1)(L^1–L^1)_{\frac{1}{2}}]$,[7] and $[Cu(HL^1)_2(L^1–L^1)_{\frac{1}{2}}Cl]$[7] [$L^1$–$L^1$ = bis(benzo-1,3-thiazol-2-yl) disulphide] and a copper(II) complex $[Cu(L^1)_2]$.[8–11] Jeannin *et al.*[4] have established that $HL^1$ in $CHCl_3$ reacts with solid $Cu(ClO_4)_2 \cdot 6H_2O$ to give an unusual copper(I) compound, characterized by *X*-ray crystallography as $[Cu(HL^1)(L^1–S–L^1)][ClO_4] \cdot 2CHCl_3$ [$L^1$–S–$L^1$ = bis(benzo-1,3-thiazol-2-yl) trisulphide]. In contrast, using pyridine as solvent we have observed the copper-promoted formation of the monosulphides of benzo-1,3-thiazoline-2-thione and its 6-ethoxy derivative.[12]

In this paper, we clarify the nature of the copper–benzo-1,3-thiazoline-2-thione reaction and find that the only valid formulations for the above amorphous precipitates are $[Cu(L^1)]$, if an aqueous ethanol system is used, and $[Cu(HL^1)_2Cl]$, if absolute ethanol is the solvent. The erroneous formulations are shown to arise from bis(benzo-1,3-thiazol-2-yl) disulphide contamination. The work has been extended by using a number of related heterocyclic thione donors ($HL^2$–$HL^6$) and diphenyldithiophosphinic acid ($HS_2PPh_2$) to provide support for these findings.







| | X | R | | X | R | |
|---|---|---|---|---|---|---|
| $HL^1$ | S | H | $HL^4$ | S | Ph | $HL^6$ |
| $HL^2$ | S | OEt | $HL^5$ | NMe | H | |
| $HL^3$ | NH | H | | | | |

In order to obtain crystalline copper–benzo-1,3-thiazoline-2-thione complexes it has been necessary to treat the insoluble amorphous $[Cu(L^1)]$ compound with chelating phosphines, and the single-crystal *X*-ray structure of one of these complexes, $[Cu_2(L^1)_2(dppe)_3]$ [dppe = 1,2-bis(diphenylphosphino)-ethane)], is reported.

## Experimental

The ligands $HL^1$ (benzo-1,3-thiazoline-2-thione), $HL^3$ (benz-1,3-imidazoline-2-thione), $HL^5$ [1-methylimidazoline-2(3*H*)-thione], $HL^6$ [pyridine-2(1*H*)-thione], and diphenyldithiophosphinic acid were obtained from Aldrich Chemical Co., $HL^2$ (6-ethoxybenzo-1,3-thiazoline-2-thione) from Alpha Products, $HL^4$ [4-phenylthiazoline-2(3*H*)-thione] from Frinton Laboratories, and the phosphines from Strem Chemicals. Infrared spectra were recorded on a Pye Unicam SP3-300 spectrometer on Nujol or hexachlorobutadiene mulls. All the complexes were dried under vacuum. Microanalyses (Table 1) were by Professor

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

**Table 1.** Analytical data for the complexes.

| Complex | Colour | Analyses (%)[a] | | | |
|---|---|---|---|---|---|
| | | C | H | N | X |
| $[Cu(HL^1)_2Cl]$ | Pale Yellow | 39.3 | 2.7 | 6.7 | 8.4[b] |
| | | (38.8) | (2.1) | (6.5) | (8.2) |
| $[Cu(HL^1)_2Br]$ | Yellow | 34.2 | 2.2 | 5.7 | |
| | | (35.3) | (1.9) | (5.9) | |
| $[Cu(HL^1)_2I]$ | Yellow | 33.0 | 2.35 | 5.3 | 23.6[c] |
| | | (32.0) | (1.9) | (5.3) | (24.2) |
| $[Cu(L^1)]$ | Orange | 36.75 | 1.9 | 6.1 | |
| | | (36.6) | (1.8) | (6.1) | |
| $[Cu(HL^2)_2Cl]$ | Tan | 42.45 | 3.75 | 5.4 | 5.55[b] |
| | | (41.45) | (3.5) | (5.35) | (6.8) |
| $[Cu(HL^2)_2Br]$ | Cream | 38.3 | 3.6 | 4.7 | 14.8[d] |
| | | (38.2) | (3.2) | (4.95) | (14.1) |
| $[Cu(L^2)]$ | Orange | 39.3 | 3.0 | 5.1 | |
| | | (39.3) | (2.9) | (5.1) | |
| $[Cu(HL^3)Br]\cdot0.5H_2O$ | White | 28.5 | 2.6 | 9.7 | |
| | | (27.8) | (2.3) | (9.3) | |
| $[Cu(HL^4)Cl]\cdot0.5H_2O$ | Yellow | 35.4 | 2.4 | 4.6 | 11.8[b] |
| | | (35.9) | (2.7) | (4.65) | (11.8) |
| $[Cu(HL^4)Br]\cdot H_2O$ | Yellow | 30.4 | 2.3 | 3.8 | 24.4[d] |
| | | (30.55) | (2.4) | (4.0) | (24.8) |
| $[Cu(L^4)]$ | White | 42.4 | 2.2 | 5.4 | |
| | | (42.25) | (2.4) | (5.5) | |
| $[Cu(HL^5)Br]$ | Yellow | 18.1 | 2.5 | 10.7 | |
| | | (18.6) | (2.25) | (10.9) | |
| $[Cu(HL^6)Br]\cdot0.5H_2O$ | Orange | 22.7 | 2.25 | 5.3 | |
| | | (22.8) | (2.3) | (5.3) | |
| $[Cu(HS_2PPh_2)Cl]$ | White | 41.0 | 3.75 | 8.6[e] | 9.2[b] |
| | | (41.3) | (3.2) | (8.9) | (10.1) |
| $[Cu(HS_2PPh_2)Br]$ | White | 36.7 | 3.3 | | 7.2[e] |
| | | (36.6) | (2.8) | | (7.9) |
| $[Cu(L^1)(dppm)]$ | Cream | 62.0 | 4.5 | 2.1 | |
| | | (62.6) | (4.3) | (2.3) | |
| $[Cu_2(L^1)_2(dppe)_3]$ | Cream | 66.5 | 5.4 | 1.65 | 11.5[e] |
| | | (66.8) | (4.9) | (1.7) | (11.2) |

[a] Calculated values are given in parentheses. [b] Cl. [c] I. [d] Br. [e] P.

A. D. Campbell, University of Otago. Some analytical figures are outside the normally accepted limits but the insoluble nature of the complexes prevented their recrystallisation.

*Preparation of the Copper Complexes.*—$[Cu(HL)_2X]$ (HL = $HL^1$ *or* $HL^2$, X = Cl *or* Br). These compounds were prepared by adding the appropriate copper(II) halide (5 mmol) dissolved in absolute ethanol (50—100 $cm^3$) dropwise to the ligand, HL (15 mmol), in the same solvent (100—350 $cm^3$). In the case of $[Cu(HL^2)_2Br]$ the $HL^2$:Cu ratio was 6:1. The resulting precipitates were filtered off and washed thoroughly with ethanol and $CHCl_3$. Yields *ca.* 70%.

$[Cu(HL)X]$ (HL = $HL^3$, $HL^5$, *or* $HL^6$, X = Br; $HL^4$, X = Cl *or* Br). The appropriate copper(II) halide (2.5 mmol) dissolved in absolute ethanol (50—80 $cm^3$) was added dropwise to the ligand, HL (5 mmol), in ethanol (50—250 $cm^3$). The products, which precipitated immediately, were filtered off and washed with ethanol and $CHCl_3$. Some of the products were obtained as hydrates (see Table 1). Yields *ca.* 90%.

$[Cu(HL^1)_2I]$. The complex $[Cu(HL^1)_2Cl]$ (0.43 g, 1 mmol) was added to a solution of KI (0.83 g, 5 mmol) dissolved in water (50 $cm^3$). The resulting slurry was refluxed for 2 h during which time the colour of the solid became more intense. The product was filtered off, washed with water, ethanol, and $CHCl_3$. Yield 80%.

$[Cu(L^1)]$. The ligand $HL^1$ (1.6 g, 10 mmol) dissolved in ethanol (120 $cm^3$) was added dropwise to $CuSO_4\cdot5H_2O$ (1.2 g, 4.5 mmol) in water (40 $cm^3$). The resulting precipitate was filtered off, washed with water, ethanol, and $CHCl_3$. Yield 0.22 g, (20%).

$[Cu(L^2)]$. The salt $Cu(NO_3)_2\cdot3H_2O$ (0.73 g, 3 mmol) in ethanol (100 $cm^3$) was added dropwise to $HL^2$ (1.27 g, 6 mmol) in ethanol (200 $cm^3$)–dimethyl sulphoxide (30 $cm^3$). After stirring for 1 h, the resulting solid was filtered off and washed with both solvents. It was recrystallised from $CH_2Cl_2$.

$[Cu(L^4)]$. The complex $[Cu(MeCN)_4][ClO_4]$ (1.0 g, 3 mmol) dissolved in MeCN was added dropwise to the ligand $HL^4$ (0.6 g, 3 mmol) in ethanol. The precipitate was washed with both solvents. Yield 0.58 g (78%).

$[Cu(HS_2PPh_2)X]$ (X = Cl *or* Br). The copper(II) halide (5 mmol) in ethanol (50—100 $cm^3$) was added dropwise to a solution of diphenyldithiophosphinic acid (12.25 mmol) dissolved in acetone (100 $cm^3$)–ethanol (150 $cm^3$). The products were washed thoroughly with ethanol, acetone, and $CHCl_3$. Yields *ca.* 70%.

$[Cu(L^1)(dppm)]$ [dppm = 1,2-*bis*(*diphenylphosphino*)*methane*]. The ligand, dppm (0.58 g, 1.5 mmol), was dissolved in hot acetone–$CH_2Cl_2$ (60:40) (50 $cm^3$) and added to a suspension of $[Cu(L^1)]$ (0.23 g, 1 mmol) in acetone (10 $cm^3$). The mixture was refluxed for 1 h. The resulting yellow solution was filtered rapidly and reduced in volume using a rotary evaporator. Upon addition of hexane the product slowly precipitated.

$[Cu_2(L^1)_2(dppe)_3]$ [dppe = 1,2-*bis*(*diphenylphosphino*)-*ethane*]. The ligand dppe (0.43 g, 1 mmol), was dissolved in hot acetone (50 $cm^3$) and added to a suspension of $[Cu(L^1)]$ (0.23 g, 1 mmol) in the same solvent (10 $cm^3$). As the mixture was gently heated a yellow solution was obtained from which the product slowly precipitated. It was filtered off and washed with acetone and diethyl ether.

*Crystal Structure Determination of* $[Cu_2(L^1)_2(dppe)_3]$.—Suitable single crystals were obtained as cream cubes from $CH_2Cl_2$ by liquid diffusion using acetone as the precipitating solvent.

*Crystal data.* $C_{92}H_{80}Cu_2N_2P_6S_4$, $M$ = 1 654.2, triclinic, $a$ = 17.334(3), $b$ = 17.348(2), $c$ = 20.110(2) Å, $\alpha$ = 82.54(1), $\beta$ = 120.73(1), $\gamma$ = 123.86(1)°, $U$ = 4214.1 $Å^3$ (by least-squares refinement from the positions of 12 reflections on the diffractometer), Cu-$K_\alpha$ radiation, $\lambda$ = 1.5418 Å, space group $P\bar{1}$, $D_m$ = 1.33 g $cm^{-3}$ (by flotation), $Z$ = 2, $D_c$ = 1.30 g $cm^{-3}$, $\mu$(Cu-$K_\alpha$) = 30.3 $cm^{-1}$

*Data collection and reduction.* Data were collected on an automated Hilger and Watts four-circle diffractometer using nickel-filtered Cu-$K_\alpha$ radiation. Using a $\theta$—$2\theta$ scan (50 steps of 0.02°, counting 1.2 s per step and a background count of 12 s on each side of each scan) reflections of $\pm h \pm kl$ were measured at $\theta < 45°$. Three standard reflections were measured every 100 reflections but no reduction in intensity was noted. From 5 258 unique reflections, 3 317 had intensities $I > 3\sigma(I)$. These were used in all subsequent calculations. Lorentz and polarisation corrections were made but no absorption correction was applied.

*Structure determination.* The structure was solved by direct methods and refined by full-matrix least-squares methods. The copper, phosphorus, and sulphur atoms and the $L^1$ anion atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions but were not refined. Phenyl rings of the dppe ligand were treated as rigid groups with C–C and C–H bond lengths of 1.395 and 1.08 Å respectively and C–C–C bond angles of 120°. Unit weights were used throughout the refinement. At convergence $R$ = 0.096 and $R'$ = 0.096. Computations employed the MULTAN 80[13] and SHELX 76[14] programs; atomic scattering factors were as defined therein. Positional parameters for non-hydrogen atoms are given in Table 2.

**Table 2.** Non-hydrogen atom co-ordinates for $[Cu_2(L^1)_2(dppe)_3]$ with standard deviations in parentheses

| Molecule 1 | | | | Molecule 2 | | | |
|---|---|---|---|---|---|---|---|
| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* | Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
| Cu(1) | 0.082 8(2) | 0.359 3(2) | 0.113 2(2) | Cu(2) | 0.746 0(2) | 0.969 2(2) | 0.386 7(2) |
| P(11) | 0.062 7(5) | 0.366 6(4) | 0.218 5(3) | P(21) | 0.647 7(5) | 0.844 6(4) | 0.281 4(3) |
| P(12) | 0.064 3(5) | 0.218 3(5) | 0.134 5(3) | P(22) | 0.583 5(5) | 0.928 5(4) | 0.365 3(3) |
| P(13) | −0.059 3(5) | 0.348 7(4) | −0.001 1(3) | P(23) | 0.850 6(5) | 0.941 5(4) | 0.501 5(3) |
| S(11) | 0.251 1(5) | 0.491 2(4) | 0.138 4(3) | S(21) | 0.853 2(5) | 0.113 0(4) | 0.361 7(3) |
| C(11) | 0.060(2) | 0.261(2) | 0.261(1) | C(21) | 0.503(2) | 0.799(2) | 0.240(1) |
| C(12) | −0.004(2) | 0.179(2) | 0.193(1) | C(22) | 0.485(2) | 0.806(2) | 0.308(1) |
| C(13) | 0.271(2) | 0.469(2) | 0.072(1) | C(23) | 0.898(2) | 1.201(2) | 0.427(1) |
| C(10) | −0.053(2) | 0.457(2) | 0.002(1) | C(20) | 0.956(2) | 0.949(1) | 0.497(1) |
| S(12) | 0.362 0(7) | 0.570 3(6) | 0.048 4(5) | S(22) | 1.022 3(7) | 1.312 8(6) | 0.451 3(5) |
| N(11) | 0.240(2) | 0.392(2) | 0.035(1) | N(21) | 0.856(2) | 1.204(2) | 0.464(1) |
| C(131) | 0.347(2) | 0.501(2) | −0.013(2) | C(231) | 1.017(2) | 1.362(2) | 0.513(2) |
| C(132) | 0.278(2) | 0.404(3) | −0.017(2) | C(232) | 0.920(3) | 1.296(3) | 0.514(2) |
| C(133) | 0.254(3) | 0.328(3) | −0.059(3) | C(233) | 0.886(4) | 1.312(3) | 0.558(2) |
| C(134) | 0.293(3) | 0.354(4) | −0.112(3) | C(234) | 0.962(5) | 1.403(3) | 0.611(2) |
| C(135) | 0.363(3) | 0.447(4) | −0.113(2) | C(235) | 1.062(4) | 1.474(3) | 0.613(2) |
| C(136) | 0.392(3) | 0.523(3) | −0.060(2) | C(236) | 1.085(3) | 1.451(2) | 0.563(2) |
| C(14) | 0.179(2) | 0.463(2) | 0.309(1) | C(24) | 0.655(2) | 0.865(2) | 0.191(1) |
| C(141) | 0.152(2) | 0.481(2) | 0.356(1) | C(241) | 0.626(2) | 0.794(2) | 0.144(2) |
| C(142) | 0.251(2) | 0.554(2) | 0.434(2) | C(242) | 0.623(2) | 0.816(2) | 0.067(2) |
| C(143) | 0.353(2) | 0.599(2) | 0.447(2) | C(243) | 0.651(2) | 0.905(2) | 0.052(2) |
| C(144) | 0.373(2) | 0.579(2) | 0.397(2) | C(244) | 0.679(2) | 0.975(2) | 0.099(2) |
| C(145) | 0.280(2) | 0.509(2) | 0.323(1) | C(245) | 0.682(2) | 0.957(2) | 0.177(2) |
| C(15) | −0.054(2) | 0.352(2) | 0.203(1) | C(25) | 0.652(2) | 0.742(2) | 0.297(1) |
| C(151) | −0.067(2) | 0.429(2) | 0.185(1) | C(251) | 0.562(2) | 0.656(2) | 0.293(1) |
| C(152) | −0.158(2) | 0.421(2) | 0.172(2) | C(252) | 0.564(2) | 0.574(2) | 0.306(2) |
| C(153) | −0.240(2) | 0.338(2) | 0.179(2) | C(253) | 0.656(2) | 0.582(2) | 0.321(2) |
| C(154) | −0.232(2) | 0.260(2) | 0.192(2) | C(254) | 0.750(2) | 0.668(2) | 0.327(2) |
| C(155) | −0.140(2) | 0.269(2) | 0.205(1) | C(255) | 0.744(2) | 0.751(2) | 0.316(1) |
| C(16) | −0.026(2) | 0.113(2) | 0.053(1) | C(26) | 0.560(2) | 0.923(2) | 0.446(1) |
| C(161) | 0.002(2) | 0.130(2) | −0.005(1) | C(261) | 0.636(2) | 1.004(2) | 0.506(1) |
| C(162) | −0.066(2) | 0.054(2) | −0.072(2) | C(262) | 0.626(2) | 1.006(2) | 0.572(1) |
| C(163) | −0.149(2) | −0.033(2) | −0.073(1) | C(263) | 0.539(2) | 0.925(2) | 0.574(1) |
| C(164) | −0.173(2) | −0.052(2) | −0.012(2) | C(264) | 0.463(2) | 0.844(2) | 0.512(2) |
| C(165) | −0.105(2) | 0.028(2) | 0.053(1) | C(265) | 0.476(2) | 0.841(2) | 0.446(1) |
| C(17) | 0.182(2) | 0.216(2) | 0.197(1) | C(27) | 0.517(2) | 0.987(2) | 0.301(1) |
| C(171) | 0.174(2) | 0.137(2) | 0.232(2) | C(271) | 0.405(2) | 0.941(2) | 0.266(1) |
| C(172) | 0.278(2) | 0.142(2) | 0.281(2) | C(272) | 0.358(2) | 0.992(2) | 0.219(2) |
| C(173) | 0.373(2) | 0.216(2) | 0.286(2) | C(273) | 0.429(2) | 1.082(2) | 0.215(2) |
| C(174) | 0.382(3) | 0.294(2) | 0.251(2) | C(274) | 0.539(3) | 1.131(2) | 0.250(2) |
| C(175) | 0.279(2) | 0.291(2) | 0.203(2) | C(275) | 0.588(2) | 1.077(2) | 0.296(2) |
| C(18) | −0.078(2) | 0.329(2) | −0.099(1) | C(28) | 0.773(2) | 0.821(1) | 0.519(1) |
| C(181) | −0.018(2) | 0.314(2) | −0.104(2) | C(281) | 0.790(2) | 0.752(2) | 0.508(1) |
| C(182) | −0.032(3) | 0.294(2) | −0.181(2) | C(282) | 0.722(2) | 0.660(2) | 0.520(1) |
| C(183) | −0.120(3) | 0.297(2) | −0.247(2) | C(283) | 0.655(2) | 0.643(2) | 0.545(1) |
| C(184) | −0.181(2) | 0.315(2) | −0.242(2) | C(284) | 0.645(2) | 0.710(2) | 0.560(2) |
| C(185) | −0.166(2) | 0.336(2) | −0.165(2) | C(285) | 0.708(2) | 0.805(2) | 0.547(1) |
| C(19) | −0.197(2) | 0.256(2) | −0.019(1) | C(29) | 0.928(2) | 1.018(2) | 0.599(1) |
| C(191) | −0.252(2) | 0.278(2) | −0.008(1) | C(291) | 1.001(2) | 1.003(2) | 0.666(2) |
| C(192) | −0.359(2) | 0.201(2) | −0.022(1) | C(292) | 1.058(2) | 1.060(2) | 0.741(2) |
| C(193) | −0.400(2) | 0.110(2) | −0.046(1) | C(293) | 1.047(2) | 1.126(2) | 0.749(2) |
| C(194) | −0.348(2) | 0.087(2) | −0.062(1) | C(294) | 0.980(3) | 1.152(2) | 0.683(2) |
| C(195) | −0.240(2) | 0.163(2) | −0.047(1) | C(295) | 0.919(2) | 1.089(2) | 0.604(2) |

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

## Results and Discussion

*The Complexes* $[Cu(HL)_2X]$ *and* $[Cu(HL)X]$.—The heterocyclic thioamides, $HL^1$–$HL^6$, react with the appropriate copper(II) halide in absolute ethanol to give copper(I) halide complexes (listed in Table 1) which contain the ligand in the neutral form. Unfortunately the insolubility of the complexes has prevented solution studies (*e.g.* n.m.r. spectroscopy) and hence their characterisation relies on analytical data. The reaction stoicheiometries can be represented by the general equations (1) ($HL = HL^1$ or $HL^2$, X = Cl or Br) and (2) ($HL = HL^3, HL^5,$ or $HL^6$, X = Br; $HL = HL^4$, X = Cl or Br).

$$CuX_2 + 3HL \longrightarrow [Cu(HL)_2X] + \tfrac{1}{2}(L\text{–}L) + HX \quad (1)$$

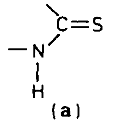
$$CuX_2 + 2HL \longrightarrow [Cu(HL)X] + \tfrac{1}{2}(L\text{–}L) + HX \quad (2)$$

Thus in all cases a disulphide (L–L) and an acid (HX), which can be determined by base titration,[15] are produced as co-products. Failure to recognise the presence of the disulphide as

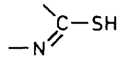
**Table 3.** Distances (Å) and angles (°) for $[Cu_2(L^1)_2(dppe)_3]$ with standard deviations in parentheses

| | Molecule 1 | Molecule 2 |
|---|---|---|
| Cu(1)–P(11) | 2.344(9) | 2.337(8) |
| Cu(1)–P(12) | 2.293(9) | 2.291(9) |
| Cu(1)–P(13) | 2.282(7) | 2.292(7) |
| Cu(1)–S(11) | 2.314(6) | 2.322(7) |
| S(11)–C(13) | 1.67(3) | 1.68(2) |
| C(13)–S(12) | 1.81(3) | 1.78(2) |
| C(13)–N(11) | 1.30(4) | 1.29(5) |
| S(12)–C(131) | 1.65(4) | 1.65(5) |
| N(11)–C(132) | 1.45(6) | 1.44(4) |
| P(11)–C(11) | 1.90(3) | 1.85(3) |
| P(12)–C(12) | 1.89(3) | 1.83(2) |
| C(11)–C(12) | 1.52(4) | 1.58(5) |
| C(10)–C(10′) | 1.64(4) | 1.54(3) |
| P(11)–Cu(1)–P(12) | 89.9(3) | 89.3(3) |
| P(11)–Cu(1)–P(13) | 108.8(4) | 109.1(3) |
| P(11)–Cu(1)–S(11) | 109.9(2) | 110.1(1) |
| P(12)–Cu(1)–P(13) | 115.5(2) | 115.6(3) |
| P(12)–Cu(1)–S(11) | 118.4(4) | 118.6(4) |
| P(13)–Cu(1)–S(11) | 111.8(3) | 111.6(2) |
| Cu(1)–S(11)–C(13) | 107(1) | 108(1) |
| S(11)–C(13)–N(11) | 134(2) | 131(2) |
| S(12)–C(13)–N(11) | 109(3) | 111(2) |
| Cu(1)–P(11)–C(11) | 102(1) | 103(1) |
| Cu(1)–P(12)–C(12) | 101(1) | 104(1) |
| P(11)–C(11)–C(12) | 109(2) | 111(1) |
| P(12)–C(12)–C(11) | 109(2) | 109(2) |
| Cu(1)–P(13)–C(10) | 111(1) | 110(1) |
| C(13)–N(11)–C(132) | 116(3) | 113(3) |
| C(13)–S(12)–C(131) | 92(2) | 93(2) |

a potential contaminant of the copper(I) complex can explain the formulation $[Cu(HL^1)_2(L^1\text{–}L^1)_{\frac{1}{2}}Cl]$.[7] Less obvious is the proposal of a diamagnetic copper(II) complex, $[Cu(L^1)_2]$, from reaction (1), but while the reported C, H, and N microanalytical data fit the formulation a chloride analysis was not obtained.[9,10] Chloroform was found to be a suitable wash solvent for disulphide removal and in the case of the $HL^1$ + $CuCl_2$ reaction the weighing of the extracted $L^1\text{–}L^1$ (mass spectrum *m/z* 332) showed the wash to be quantitative. This procedure has also allowed us to reformulate the compound '$[Cu(HL^6)_2Br_2]$,' prepared by Evans and Wilkinson,[16] as $[Cu(HL^6)Br]$. While the analogous copper(I) chloride complex of $HL^6$ can be isolated, *viz.* $[Cu(HL^6)Cl]$,[16,17] a second compound has also been reported. This is a binuclear complex, $[Cu_2(HL^6)_6]Cl_2$, containing both terminal and bridging $HL^6$ ligands in the thione form (**a**).[17] The single-crystal *X*-ray structure of the 1:1 copper(I) chloride complex of $HL^5$ shows it to be a dimer $[Cu_2(HL^5)_4Cl_2]$ with the ligand in the thione form again bound in both bridging and terminal modes.[18] This and other structural data,[1,5] as well as the presence of a ν(NH) stretching frequency in the i.r. spectra of all the complexes, indicate the preference of the neutral HL ligands for the thione (**a**) rather than the thiol (**b**) tautomer, when bound to copper(I).



(**a**)



(**b**)

*The Complexes* [CuL].—Using aqueous ethanol or other mixed solvent systems, deprotonated ligand complexes are obtained [equation (3) ($HL = HL^1$, $X = \frac{1}{2}SO_4$; $HL = HL^2$, $X = NO_3$)]. Again from the reaction stoicheiometry, it is

$$CuX_2 + 2HL \longrightarrow [CuL] + \tfrac{1}{2}(L\text{–}L) + 2HX \qquad (3)$$

apparent how the presence of insoluble disulphide can explain such erroneous formulations as $[Cu(L^1)(L^1\text{–}L^1)_{\frac{1}{2}}]$,[7] $[Cu(L^1)(HL^1)]$,[6] and the 'cupric' complex $[Cu(L^1)_2]$.[8] An *X*-ray photoelectron spectroscopic study shows the $Cu(2p_{\frac{3}{2}})$ binding energy for the 'cupric complex' to be consistent with the copper(I) state and the same as for a pure sample of $[Cu(L^1)]$.[7] The [CuL] complexes are probably polymeric with ligands in the deprotonated 'thiol' form (**b**) bridging the copper atoms. The photoelectron spectrum of $[Cu(L^1)]$ points to both exocyclic sulphur and nitrogen co-ordination.[7] Tetrameric units have been proposed, from a mass spectral study, for $[Cu(L^6)]$.[17]

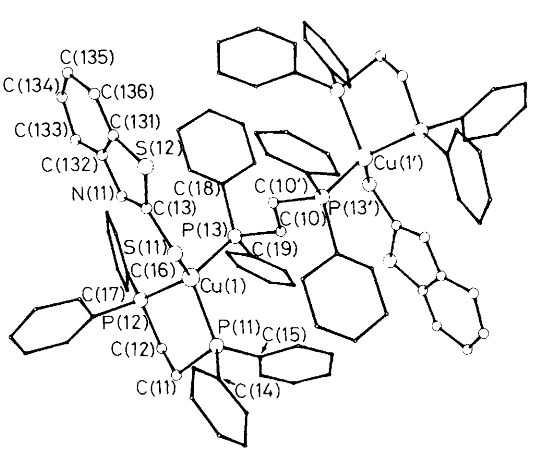


**Figure.** The structure of $[Cu_2(L^1)_2(dppe)_3]$ showing the numbering system used

*The Complexes* $[Cu(HS_2PPh_2)X]$.—Even though diphenyldithiophosphinic acid is not a thioamide its reaction with copper(II) salts is of note as it produces colourless copper(I) derivatives $[Cu(HS_2PPh_2)X]$ (X = Cl or Br) by reactions analogous to equation (2). These complexes are unusual in that the acid has not been deprotonated to give a compound of the expected type, *viz.* $[\{Cu(S_2PR_2)\}_4]$.[19]

*The Reaction of* $[Cu(L^1)]$ *with Diphosphines*.—The insoluble compound $[Cu(L^1)]$ dissolves in hot acetone solutions of the diphosphine ligands, dppm and dppe. Analytical data for the compounds isolated, $[Cu(L^1)(dppm)]$ and $[Cu_2(L^1)_2(dppe)_3]$, are given in Table 1. I.r. spectra indicated the presence of both the phosphine and anionic $L^1$ ligands, the latter being confirmed by the single-crystal *X*-ray structure on the dppe complex.

*Crystal Structure of* μ-[1,2-*bis*(*diphenylphosphino*)*ethane*]-*bis*{(*benzo*-1,3-*thiazole*-2-*thiolato*-S)[1,2-*bis*(*diphenylphosphino*) *ethane*]*copper*(I)}, $[Cu_2(L^1)_2(dppe)_3]$.—The complex is a centrosymmetric dimer with the centre of symmetry between the two methylene carbons of a bridging dppe ligand. The distorted tetrahedral co-ordination sphere of each copper atom is completed by a chelating dppe ligand and an anionic $L^1$ ligand binding through the exocyclic sulphur atom. There are two similar independent molecules in the unit cell. A view of the dimer is shown in the Figure and selected bond lengths and angles are in Table 3.

The Cu–P distances (mean 2.306 Å) are comparable to those found in other copper(I) complexes containing three Cu–P bonds[20–23] and the mean Cu–S distance (2.318 Å) compares well with other four-co-ordinate complexes with similar copper(I)– thiolate interactions.[1,17,24] Bond angles around the

**Table 4.** Selected structural parameters for $[Cu_2(L^1)_2(dppe)_3]$ *

Distance of Cu(1) from tetrahedral faces

| Face | Distance (Å) | Face | Distance (Å) |
|---|---|---|---|
| P(11)–P(12)–P(13) | 0.92 | P(11)–P(13)–S(11) | 0.74 |
| P(11)–P(12)–S(11) | 0.88 | P(12)–P(13)–S(11) | 0.51 |

Dihedral angles between planes about Cu(1)

| Plane 1 | Plane 2 | Angle (°) |
|---|---|---|
| P(11)–Cu(1)–P(12) | P(13)–Cu(1)–S(11) | 90.5 |
| P(11)–Cu(1)–P(13) | P(12)–Cu(1)–S(11) | 79.8 |
| P(12)–Cu(1)–P(13) | P(11)–Cu(1)–S(11) | 100.5 |
| P(11)–Cu(1)–P(12) | C(11)–Cu(1)–C(12) | 32.5 |

Least-squares plane for atoms S(11), C(13), S(12), N(11), C(131), C(133), C(134), C(135), and C(136)

$$-0.6483X + 0.1257Y - 0.7509Z - 0.2395 = 0$$

Distances (Å) of atoms from plane

| | | | | | |
|---|---|---|---|---|---|
| S(11) | 0.013 | C(131) | 0.001 | C(134) | 0.049 |
| C(13) | 0.036 | C(132) | −0.016 | C(135) | 0.041 |
| S(12) | −0.018 | C(133) | −0.061 | C(136) | −0.039 |
| N(11) | −0.004 | | | | |

* For molecule 1.

copper atom show the distorted tetrahedral geometry is a reflection of the small bite of the chelating dppe ligand [P(11)–Cu(1)–P(12) 89.9(3)°]. The remaining bond angles [108.8(4)—118.6(4)°] also show deviations from the ideal tetrahedral angle, indicating considerable steric crowding. The distortion is also reflected in the distances of the copper atom from the four faces of the co-ordination tetrahedron (Table 4).

The $L^1$ anion can be regarded as being in the deprotonated thiol form (**b**) although typically[25] the mean exocyclic C(13)–S(11) bond distance at 1.68 Å is shorter than expected for a single bond (*ca.* 1.80 Å) indicating some conjugation between this bond and the ring. Other $L^1$ bond distances and angles are normal[25,26] with the entire ligand being planar with only very small deviations of the atoms out of the plane (Table 4). The C(131) and C(132) atoms are 0.09 and 0.06 Å above the S(12)–C(13)–N(13) plane respectively and the torsion angle about the C(131)–C(132) bond is 1.7°.

The presence of the crystallographic centre of symmetry between the two methylene carbon atoms of the bridging dppe ligand constrains the atoms P(13), C(10), C(10′), and P(13′) to be coplanar with the chain adopting a *trans* configuration. The distance between the two copper atoms is 7.02 Å and they are 2.01 Å above and below the P–C–C–P plane. As discussed elsewhere,[20–22] these values, along with the value of the rotation angle (69.7°) about C(10)–P(13), indicate that the conformation of the bridging chain is close to being the most energetically favourable.

The five-membered chelating dppe ring is non-planar and asymmetric, this deviation being manifested by the displacements of C(11) and C(12) by 0.19 and 0.62 Å above and below the P(11)–Cu(1)–P(12) plane respectively. Theoretical calculations on the conformational energies of five-membered chelate rings have shown the actual conformation is dependent on the torsion angle (ω) about the C(11)–C(12) bond.[27] The value of ω for $[Cu_2(L^1)_2(dppe)_3]$ is 59.2° and compares favourably to that found for related complexes and close to the value (60°) expected for an ideally staggered conformation.

It is apparent that the compound $[Cu_2(L^1)_2(dppe)_3]$ is one of a series of structurally related $Cu^I$–dppe compounds of the type $[Cu_2A_2(dppe)_3]$ {where A is a monoanion such as Cl,[22] $N_3$,[20] $CF_3CN_4$ (5-trifluoromethyl-1,2,3,4-tetrazolate),[21] or OPh[23]}. Such a stoicheiometry must allow the chelated and bridged dppe ligands to achieve minimum energy conformations and in doing so create a cavity into which various anions can be accommodated on co-ordination to the copper.

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