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Mononuclear and Binuclear Cu(I) Complexes with Metal–Sulfur Ligation

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Abstract

The synthesis, characterization and electrochemistry of the copper(I)(triphenylphosphine)-chloride, bromide and iodide complexes of pyridine-2-thione (py2SH), pyridine-4-thione (py4SH) and pyrimidine-2-thione (pymtH) and the crystal structure of the complex $[Cu(py2SH)(PPh_3)Br]_2$ are reported. Crystals of $[Cu(py2SH)(PPh_3)Br]_2$ are triclinic, space group $P\bar{1}$, with $a = 9.586(4)$, $b = 9.562(5)$, $c = 13.573(5)$ Å, $\alpha = 77.56(3)$, $\beta = 73.32(3)$, $\gamma = 62.38(3)°$ and $Z = 1$. The molecule contains a planar Cu_2S_2 moiety with bond lengths Cu(1)–S(1) = 2.383 Å and Cu(1)–S(1′) = 2.392 Å and bond angles S–Cu–S = 88.5° and Cu–S–Cu′ = 91.5°. The structure has been solved by direct methods with a final R of 0.039. The complex is binuclear, the stereochemistry of the Cu_2S_2 core is strictly planar. The equivalent copper atoms have pseudotetrahedral geometry. The electrochemical study indicates that the potentials are in the range of about +0.3 to +1.1 V *versus* SCE. The synthesis and structure determination at 140 K of $Cu(py2SH)(PPh_3)_2Br$ is also reported. Crystals are monoclinic, space group $P2_1/n$, with $a = 9.436(3)$, $b = 19.168(5)$, $c = 19.597(5)$ Å, $\beta = 91.31(3)°$ and $Z = 4$. The metal ion has a distorted tetrahedral geometry with bond lengths Cu–S = 2.302, Cu–Br = 2.462 and Cu–P = 2.263–2.267 Å. The structure has been solved by direct methods with a final R of 0.075.

Introduction

Heterocyclic thiones as ligands in metal complexes have attracted considerable attention because of their relevance to biological systems [1]. Our previous research was concentrated on complexes formed by pyridine-2-thione. We reported the crystal structures of mononuclear $[Cu(py2SH)_4]NO_3$ [2], $[Cu(py2SH)_4]ClO_4$ [3] and binuclear $[Cu(py2SH)_4X]_2$ [4] complexes with four-coordinated copper in the solid state. Recently, the structure of $(PPh_3)_2Cu(\mu\text{-}SPh)_2Cu(PPh_3)_2$, as the first example of doubly bridging thiolate with planar stereochemistry at sulfur has been reported by Dance *et al.* [5]. In order to investigate the stereochemical properties of bridging or non-bridging heterocyclic thiones in copper complexes with bulky ligands (PPh_3) we prepared and structurally characterized the complexes $(PPh_3)(Br)Cu(\mu\text{-}py2SH)_2Cu(Br)(PPh_3)$ and $(PPh_3)_2(Br)(py2SH)Cu$. We also report the synthesis, characterization and electrochemical study of a series of binuclear copper complexes of the general formula $[Cu(L)(PPh_3)(X)]_2$ (X = Cl, Br, I; L = pyridine-2-thione (py2SH), pyridine-4-thione (py4SH), pyrimidine-2-thione (pymtH)). Using PPh_3 as ligand we increased the low solubility of $[Cu(py2SH)X]_2$ [4] complexes and the study (UV–Vis, ^1H NMR, CV) of the prepared complexes in solution became possible.

Experimental

Reagents

$[Cu(PPh_3)X]_4$ was prepared from CuX and PPh_3 by the method of Costa *et al.* [6]. $Cu(PPh_3)_3Br$ was prepared from CuBr and PPh_3 by the method of Lippard *et al.* [7]. $Zr(py2S)_4$ [8] was used for the preparation of the $Cu(py2SH)(PPh_3)_2Br$ complex. PPh_3, C_5H_5NS (py2SH, py4SH) were supplied by EGA; $C_4H_4N_2S$ (pymtH) was supplied by Merck. All thiones were used after recrystallization from ethanol.

Physical Measurements

Infrared spectra (200–4000 cm^{-1}) were recorded on a Perkin-Elmer 467 infrared spectrometer with samples prepared as KBr pellets. UV–Vis spectra were recorded on a Cary 17 UV/Vis/Near IR dual beam spectrophotometer. ^1H NMR spectra were recorded on a Bruker AW 80 spectrometer. Room temperature magnetic measurements were carried out by Faraday's method using mercury tetrathiocyanato-

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cobaltate(II) as a calibrant. Electrochemical measurements were made using a Bank Electronic Wenking PGS 81 Potentio-Galvano-Scan and a Philips PM 8143 X-Y recorder. Cyclic voltammetric measurements were performed at 23 ± 2 °C in the designated solvent under nitrogen with the electroactive component at 10^{-3} M. Tetraethylammonium perchlorate (0.1 M) was used as the supporting electrolyte. A three electrode configuration was employed, using SCE reference and platinum or carbon working and platinum auxiliary electrodes. The ferrocene/ferrocenium couple was used as an external standard. Acetonitrile as a high purity solvent was purchased from Merck Co. and was stored under dry nitrogen.

Preparation of the Complexes

$[Cu(py2SH)(PPh_3)X]_2$ (X = Cl, Br, I)

0.5 mmol of $[Cu(PPh_3)X]_4$ was dissolved in 30 ml hot toluene, and 2 mmol of py2SH in 15 ml toluene were added dropwise under stirring, generating a deep orange solution. This solution was stirred under nitrogen for 30 min after which the color changed to pale yellow. The solution was cooled to –5 °C, and a yellow microcrystalline product was deposited which was collected by filtration. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of $[Cu(py2SH)(PPh_3)Br]_2$ in $CHCl_3$.

$[Cu(py4SH)(PPh_3)X]_2$ (X = Cl, Br, I)

0.5 mmol of $[Cu(PPh_3)X]_4$ was dissolved in 50 ml of CH_2Cl_2, and 2 mmol of py4SH dissolved in 20 ml of CH_2Cl_2 were added under stirring. The solution was stirred for 24 h under nitrogen, after which time the orange color of the solution changed to pale yellow. The solution was reduced in volume to about 1/3 and 20 ml of ether were added. A yellow microcrystalline product was collected by filtration.

$[Cu(pymtH)(PPh)X]_2$ (X = Cl, Br, I)

0.5 mmol of $[Cu(PPh_3)X]_4$ and 2 mmol of pymtH were added to 60 ml toluene, and the reaction mixture was refluxed under nitrogen for 20 min. The deep red solution was reduced in volume to 20 ml and cooled to 0 °C. An orange microcrystalline product was collected by filtration. It was recrystallized from $CHCl_3$/hexane.

$Cu(py2SH)(PPh_3)_2Br$

5 mmol (0.265 g) of $Zr(py2S)_4$ were dissolved in 50 ml THF, and the solution was added to 50 ml of a 20 mmol (1.86 g) solution of $Cu(PPh_3)_3Br$ in THF. The resulting mixture was refluxed for 2 h under nitrogen. Upon cooling to room temperature a white solid was deposited which was removed by filtration. The yellow solution was reduced in volume and petroleum ether (30 ml) was layered onto it. The mixture was placed in the refrigerator overnight. The yellow crystals that deposited were collected by filtration and used in the subsequent crystal structure analysis.

The analytical data for the new compounds, melting points, and the ν(N–H) absorption bands in their IR spectra are given in Table 1.

Collection and Reduction of X-ray Data

Suitable crystals of $[Cu(py2SH)(PPh_3)Br]_2$ and $Cu(py2SH)(PPh_3)_2Br$ were obtained as described above. Crystals were mounted in glass capillaries and sealed under nitrogen. Diffraction experiments were performed at 140 K using an LT-1 liquid nitrogen cooling unit on a Syntex $P2_1$ four-circle diffractometer. Intensity data were obtained using Mo Kα (λ = 0.71069 Å) radiation monochromatized from a graphite crystal whose diffraction was parallel to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections. The

TABLE 1. Analytical Data[a], Melting Points and N–H Stretching Frequencies of the Complexes

Compound	Melting point (°C)	Analysis (%)				ν(N–H) (cm^{-1})
		C	H	N	Cu	
$[Cu(py2SH)(PPh_3)Cl]_2$	196–199	58.35 (58.47)	4.10 (4.26)	2.71 (2.96)	12.91 (13.44)	3160
$[Cu(py2SH)(PPh_3)Br]_2$	207–209	53.27 (53.44)	3.64 (3.90)	2.29 (2.71)	12.10 (12.29)	3158
$[Cu(py2SH)(PPh_3)I]_2$	210–212	47.99 (48.99)	3.57 (3.57)	1.99 (2.48)	11.83 (11.26)	3150
$[Cu(py4SH)(PPh_3)Cl]_2$	192–193	57.65 (58.47)	4.26 (4.26)	2.61 (2.96)	12.96 (13.44)	3170
$[Cu(py4SH)(PPh_3)Br]_2$	173–174	53.26 (53.44)	3.86 (3.90)	3.02 (2.71)	11.96 (12.29)	3175
$[Cu(py4SH)(PPh_3)I]_2$	180–182	48.30 (48.99)	3.30 (3.57)	2.68 (2.48)	11.40 (11.26)	3170
$[Cu(pymtH)(PPh_3)Cl]_2$	181–182	55.75 (55.81)	4.01 (4.04)	5.16 (5.91)	12.90 (13.42)	3140
$[Cu(pymtH)(PPh_3)Br]_2$	188	51.10 (51.02)	4.00 (3.69)	5.16 (5.40)	12.30 (12.27)	3140
$[Cu(pymtH)(PPh_3)I]_2$	158–160	46.62 (46.77)	3.48 (3.39)	4.78 (4.95)	11.54 (11.48)	3138
$Cu(py2SH)(PPh_3)_2Br$	191	63.90 (63.11)	4.57 (4.61)	1.78 (1.79)	8.35 (8.14)	3140

[a] Calculated values in parentheses.

TABLE 2. Experimental Details of the X-ray Diffraction Studies

	$[Cu(py2SH)(PPh_3)Br]_2$	$Cu(py2SH)(PPh_3)_2Br$
Formula	$C_{46}H_{40}N_2Br_2P_2S_2Cu_2$	$C_{41}H_{35}NBrP_2SCu$
Formula weight	1034.9	778.5
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	9.586(4)	9.436(3)
b (Å)	9.562(5)	19.168(5)
c (Å)	13.573(5)	19.597(5)
α (°)	77.56(3)	
β (°)	73.32(3)	91.31(3)
γ (°)	62.38(3)	
V (Å^3)	1051.0	3543.7
Z	1	4
D_x (g cm^{-3})	1.63	1.46
Temperature (K)	140	140
Crystal dimensions (mm)	0.21 × 0.62 × 0.05	0.21 × 0.12 × 0.04
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
Scan speed, intensity dependent (° min^{-1})	4–30	3–20
Scan mode	θ–2θ	θ–2θ
Scan range	$4° < 2\theta < 52°$	$4° < 2\theta < 50°$
No. independent reflections	2701	4992
No. reflections with $I > 2.0\sigma(I)$	2245	2045
No. variables	134	215
$R_1{}^a$, $R_2{}^{b,c}$	0.0389, 0.0410	0.0751, 0.0599

$^aR_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^bR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. ^{c}Weighting scheme: $w = [\sigma(F_o)^2 + (0.015|F_o|)^2]^{-1}$, $\sigma(F_o) = \sigma(I)/(2|F_o|Lp)$.

crystal and machine parameters used in the unit cell determination and in data acquisition are summarized in Table 2. Intensity data were collected using $\theta/2\theta$ scans with $4° < 2\theta < 52°$ for $[Cu(py2SH)(PPh_3)Br]_2$ and $4° < 2\theta < 50°$ for $Cu(py2SH)(PPh_3)_2Br$. Empirical absorption corrections were applied to both data sets on the basis of Ψ scans of selected reflections. All calculations were done using G. M. Sheldrick's SHELXTL program package. The structures were solved using the direct methods program MULTAN. Atomic scattering factors were taken as compiled in the International Tables for X-ray Crystallography [9]. For the molecules $[Cu(py2SH)(PPh_3)Br]_2$ and $Cu(py2SH)(PPh_3)_2Br$ the coordinates of the H atoms were calculated and included in the refinement using a riding model with fixed C–H distances of 0.96 Å and temperature factors fixed at values 20% higher than those of the adjacent C atoms. Experimental data on the refinement and final R indices are given in Table 2.

Results and Discussion

Synthesis and Reactivity of Complexes

The synthesis of $Cu(RSH)(PPh_3)X_2$ ($R = C_5H_5N$, $C_4H_3N_2$) can be achieved via the reaction of $Cu_4(PPh_3)_4X_4$ ('cubane' for X = Cl and 'step like' for X = Br, I) with py2SH, py4SH or pymtH in toluene or CH_2Cl_2. All the dimeric complexes are very soluble in CH_2Cl_2 or $CHCl_3$, soluble in CH_3CN, CH_3OH, THF, but insoluble in water, ether, hexane. Crystals of $[Cu(py2SH)(PPh_3)Br]_2$ suitable for X-ray analysis are formed by slow evaporation of a $CHCl_3$ solution.

The synthesis of $Cu(py2SH)(PPh_3)_2Br$ can be achieved via the reaction of $Cu(PPh_3)_3Br$ with $Zr(py2S)_4$ in THF. Although the pyridinethiol ligand is deprotonated in the Zr complex, it is protonated in the Cu complex. The $Cu(py2SH)(PPh_3)_2Br$ complex forms yellow crystalline needles being very soluble in THF, CH_2Cl_2 and CH_3CN, but insoluble in petroleum ether. Crystals suitable for X-ray diffraction were obtained from THF/petroleum ether. Attempts to isolate $Cu(py2SH)(PPh_3)_2Br$ by direct reaction of the dimer with excess of PPh_3 were unsuccessful.

All the complexes are diamagnetic in the solid state. The UV–Vis spectra of these compounds in $CHCl_3$ solution, as expected, show only UV absorption bands at 360–365 nm (ϵ = 15 000–20 000) and 260–290 nm (ϵ = 25 000–30 000) which can be assigned as intraligand transitions.

Descriptions of Structures

Parameters for data collection are given in Table 2. Fractional atomic coordinates for $[Cu(py2SH)(PPh_3)Br]_2$ and $Cu(py2SH)(PPh_3)_2Br$ are given in Tables 3 and 4 respectively. Tables 5 and 6 show interatomic distances and valence angles for the complexes $[Cu(py2SH)(PPh_3)Br]_2$ and $Cu(py2SH)(PPh_3)_2Br$ respectively.

TABLE 3. $C_{46}H_{40}N_2Br_2P_2S_2Cu_2$: Coordinates and Coefficients of the Temperature Factors of the Non-hydrogen Atoms

	x	*y*	*z*	*U* (Å^2)
Cu(1)	0.41687(9)	0.41843(7)	0.44643(4)	0.0171(4)
Br(1)	0.32330(7)	0.22326(6)	0.54735(4)	0.0206(3)
S(1)	0.3169(2)	0.6407(1)	0.5413(1)	0.0169(7)
P(1)	0.4216(2)	0.4495(1)	0.2781(1)	0.0139(7)
N(1)	0.2938(6)	0.9193(5)	0.4415(3)	0.021(1)
C(1)	0.6075(7)	0.2965(5)	0.2125(4)	0.017(1)
C(2)	0.6460(7)	0.1400(5)	0.2538(4)	0.019(1)
C(3)	0.7871(7)	0.0189(6)	0.2090(4)	0.021(1)
C(4)	0.8912(7)	0.0528(6)	0.1255(4)	0.023(1)
C(5)	0.8549(7)	0.2082(6)	0.0847(4)	0.024(1)
C(6)	0.7108(7)	0.3295(6)	0.1275(4)	0.022(1)
C(7)	0.2670(7)	0.4424(5)	0.2290(4)	0.017(1)
C(8)	0.1087(7)	0.5078(6)	0.2847(4)	0.023(1)
C(9)	−0.0142(8)	0.5180(6)	0.2455(4)	0.031(1)
C(10)	0.0192(8)	0.4617(6)	0.1527(4)	0.032(1)
C(11)	0.1762(7)	0.3928(6)	0.0982(4)	0.025(1)
C(12)	0.3003(7)	0.3842(6)	0.1357(4)	0.021(1)
C(13)	0.4305(7)	0.6326(5)	0.2112(3)	0.014(1)
C(14)	0.5180(7)	0.6873(6)	0.2454(4)	0.021(1)
C(15)	0.5277(8)	0.8274(6)	0.2016(4)	0.026(1)
C(16)	0.4485(7)	0.9161(6)	0.1233(4)	0.024(1)
C(17)	0.3640(7)	0.8615(6)	0.0881(4)	0.024(1)
C(18)	0.3541(7)	0.7211(6)	0.1315(4)	0.021(1)
C(19)	0.2355(7)	0.8098(5)	0.4620(4)	0.016(1)
C(20)	0.1063(8)	0.8423(6)	0.4178(4)	0.026(1)
C(21)	0.0444(8)	0.9812(6)	0.3567(4)	0.030(1)
C(22)	0.1097(7)	1.0889(6)	0.3382(4)	0.027(1)
C(23)	0.2349(8)	1.0571(6)	0.3812(4)	0.025(1)

Definition of the isotropic temperature factor: $\exp[-8\pi^2 U (\sin^2\theta/\lambda^2)]$. For Cu, Br, S and P the U_{eq} values calculated from the anisotropic temperature factors are given.

TABLE 4. $C_{41}H_{35}NBrP_2SCu$: Coordinates and Coefficients of the Temperature Factors of the Non-hydrogen Atoms

	x	*y*	*z*	*U* (Å^2)
Cu(1)	0.1753(2)	0.6263(1)	0.7497(1)	0.0188(6)
Br(1)	0.0550(2)	0.7403(1)	0.7496(1)	0.0263(6)
S(1)	0.4186(4)	0.6316(2)	0.7447(2)	0.025(2)
P(1)	0.1333(4)	0.5813(2)	0.8540(2)	0.018(2)
P(2)	0.1131(4)	0.5750(2)	0.6492(2)	0.022(2)
N(1)	0.3998(11)	0.7688(6)	0.7361(5)	0.024(3)
C(1)	0.1844(14)	0.6370(7)	0.9263(7)	0.017(4)
C(2)	0.3203(15)	0.6598(7)	0.9308(7)	0.019(4)
C(3)	0.3664(18)	0.7000(8)	0.9858(7)	0.030(4)
C(4)	0.2767(17)	0.7183(8)	1.0341(9)	0.040(5)
C(5)	0.1390(18)	0.6968(8)	1.0316(8)	0.036(5)
C(6)	0.0926(16)	0.6546(7)	0.9776(7)	0.028(4)
C(7)	0.2326(15)	0.5027(8)	0.8722(8)	0.023(4)
C(8)	0.2939(15)	0.4711(7)	0.8171(8)	0.026(4)
C(9)	0.3732(16)	0.4108(7)	0.8274(8)	0.027(4)
C(10)	0.3974(15)	0.3840(8)	0.8921(7)	0.029(4)
C(11)	0.3380(16)	0.4169(8)	0.9463(8)	0.034(5)
C(12)	0.2552(15)	0.4763(7)	0.9359(8)	0.028(4)
C(13)	−0.0491(14)	0.5584(7)	0.8686(7)	0.014(4)
C(14)	−0.0971(14)	0.4937(7)	0.8843(7)	0.021(4)
C(15)	−0.2391(15)	0.4789(8)	0.8882(7)	0.031(5)
C(16)	−0.3391(16)	0.5302(7)	0.8763(7)	0.030(4)
C(17)	−0.2907(15)	0.5954(8)	0.8630(7)	0.025(4)
C(18)	−0.1482(14)	0.6098(7)	0.8557(7)	0.022(4)
C(19)	−0.0770(14)	0.5742(7)	0.6322(7)	0.014(4)
C(20)	−0.1336(15)	0.5989(7)	0.5685(7)	0.023(4)
C(21)	−0.2783(16)	0.5952(7)	0.5601(8)	0.026(4)
C(22)	−0.3641(16)	0.5694(8)	0.6076(7)	0.028(4)
C(23)	−0.3082(15)	0.5443(7)	0.6687(7)	0.023(4)
C(24)	−0.1628(15)	0.5479(7)	0.6804(8)	0.027(4)
C(25)	0.1640(15)	0.4854(7)	0.6366(7)	0.026(4)
C(26)	0.3039(14)	0.4662(7)	0.6463(6)	0.014(4)
C(27)	0.3480(17)	0.3987(8)	0.6380(7)	0.031(5)
C(28)	0.2544(16)	0.3486(8)	0.6183(7)	0.028(4)
C(29)	0.1121(16)	0.3660(8)	0.6084(8)	0.032(5)
C(30)	0.0681(15)	0.4351(7)	0.6149(6)	0.018(4)
C(31)	0.1895(14)	0.6182(7)	0.5766(7)	0.021(4)
C(32)	0.2109(15)	0.6898(8)	0.5799(8)	0.028(4)
C(33)	0.2726(15)	0.7235(8)	0.5246(7)	0.035(5)
C(34)	0.3097(17)	0.6875(8)	0.4662(8)	0.043(5)
C(35)	0.2903(16)	0.6169(8)	0.4656(8)	0.035(5)
C(36)	0.2303(15)	0.5818(8)	0.5189(7)	0.030(4)
C(37)	0.4852(15)	0.7130(7)	0.7359(7)	0.023(4)
C(38)	0.6308(16)	0.7264(8)	0.7283(7)	0.034(5)
C(39)	0.6792(17)	0.7919(8)	0.7243(7)	0.032(5)
C(40)	0.5848(15)	0.8481(8)	0.7282(7)	0.030(5)
C(41)	0.4471(17)	0.8348(8)	0.7330(7)	0.034(5)

Definition of the isotropic temperature factor: $\exp[-8\pi^2 U (\sin^2\theta/\lambda^2)]$. For Cu, Br, S and P the U_{eq} values calculated from the anisotropic temperature factors are given.

Crystal structure of [Cu(py2SH)(PPh$_3$)Br]$_2$

The molecule di(μ-pyridine-2-thione)bis(bromotriphenylphosphine)dicopper(I), as shown in Fig. 1, has a crystallographic center of symmetry that requires the Cu_2S_2 moiety to be strictly planar. The copper atoms have a distorted tetrahedral geometry. Pyridine-2-thione molecules are monodentate with the sulfur atoms as bridging coordinating groups. The two other positions of the tetrahedron are occupied by P of triphenylphosphine and Br atoms. The angles within the central Cu_2S_2 unit, S–Cu–S′ = 88.5° and Cu–S–Cu′ = 91.5° are distinctly different from those in $(PPh_3)_4Cu_2(SPh)_2$ [5], $Cu_2(mimtH)_4Cl_2$ [10a] (mimtH = 1-methylimidazoline-2(3H)-thione) and $Cu_2(py2SH)_6X_2$ (X = Cl, Br) [4] with a similar Cu_2S_2 core. Here, it is very close to a square. Structures with a similar (d^{10}) bridge region are $[Cl_2Zn(\mu\text{-}Cl)_2\text{-}ZnCl_2]^{2-}$ (Zn–Cl–Zn = 87.5°, Cl–Zn–Cl = 92.5°, Zn–Cl = 2.455, Zn–Cl′ = 2.319 Å) [11] and [Cu(purinium-6-thione)Cl_2]$_2$ (Cu–S–Cu′ = 87.5°, S–Cu–S′ = 92.9°, Cu–S = 2.253 Å, Cu–S′ = 2.734 Å) [10a, b, c]. In the two latter structures the cores Zn_2Cl_2 and Cu_2S_2 are almost orthogonal parallelograms. The Cu–P distance 2.229 Å is significantly shorter than those in $[Cu(\mu\text{-}SPh)(PPh_3)_2]_2$ (Cu–P = 2.308 Å) but in the middle of the range of values reported for $(PPh_3)Cu_2Cl_2 \cdot C_6H_6$ (2.183–2.265 Å) [7]. The Cu–Br distance at 2.431 Å is significantly

TABLE 5. $C_{46}H_{40}N_2Br_2P_2S_2Cu_2$: Interatomic Distances (Å) and Valence Angles (°)

Cu(1)–Br(1)	2.431(1)	Br(1)–Cu(1)–S(1)	110.2(1)
Cu(1)–S(1)	2.383(1)	Br(1)–Cu(1)–S(1′)	112.8(1)
Cu(1)–S(1′)	2.392(2)	Br(1)–Cu(1)–P(1)	114.8(1)
Cu(1)–P(1)	2.229(1)	S(1)–Cu(1)–S(1′)	88.5(1)
		S(1)–Cu(1)–P(1)	121.3(1)
		S(1′)–Cu(1)–P(1)	106.0(1)
Cu(1)–Cu(1′)	3.420(3)		
Br(1)... S(1)	3.947(3)		
Br(1)... S(1′)	4.017(3)		
Br(1)... P(1)	3.928(3)		
S(1)... S(1′)	3.332(3)		
S(1)... P(1)	4.021(3)		
S(1′)... P(1)	3.693(3)		
S(1)–C(19)	1.716(4)	Cu(1)–S(1)–Cu(1′)	91.5(1)
		Cu(1)–S(1)–C(19)	108.1(2)
		Cu(1)–S(1)–Cu(1′)	113.0(3)
P(1)–C(1)	1.828(4)	Cu(1)–P(1)–C(1)	109.8(2)
P(1)–C(7)	1.824(8)	Cu(1)–P(1)–C(7)	122.5(2)
P(1)–C(13)	1.818(5)	Cu(1)–P(1)–C(13)	114.2(2)
		C(1)–P(1)–C(7)	102.7(3)
		C(1)–P(1)–C(13)	103.0(2)
		C(7)–P(1)–C(13)	102.4(3)
C(1)–C(2)	1.391(7)	P(1)–C(1)–C(2)	117.2(4)
C(2)–C(3)	1.386(6)	P(1)–C(1)–C(6)	123.3(4)
C(3)–C(4)	1.370(8)	C(2)–C(1)–C(6)	119.4(4)
C(4)–C(5)	1.383(7)	C(1)–C(2)–C(3)	120.0(5)
C(5)–C(6)	1.392(6)	C(2)–C(3)–C(4)	120.3(5)
C(6)–C(1)	1.374(7)	C(3)–C(4)–C(5)	120.1(4)
		C(4)–C(5)–C(6)	119.7(5)
		C(5)–C(6)–C(1)	120.4(4)
C(7)–C(8)	1.390(7)	P(1)–C(7)–C(8)	118.0(5)
C(8)–C(9)	1.382(11)	P(1)–C(7)–C(12)	122.5(5)
C(9)–C(10)	1.371(9)	C(8)–C(7)–C(12)	119.4(7)
C(10)–C(11)	1.378(8)	C(7)–C(8)–C(9)	119.9(5)
C(11)–C(12)	1.386(11)	C(8)–C(9)–C(10)	120.5(6)
C(12)–C(7)	1.387(8)	C(9)–C(10)–C(11)	120.0(7)
		C(10)–C(11)–C(12)	120.0(6)
		C(11)–C(12)–C(7)	120.1(5)
C(13)–C(14)	1.389(11)	P(1)–C(13)–C(14)	116.6(4)
C(14)–C(15)	1.377(8)	P(1)–C(13)–C(18)	124.8(6)
C(15)–C(16)	1.379(8)	C(14)–C(13)–C(18)	118.6(5)
C(16)–C(17)	1.371(11)	C(13)–C(14)–C(15)	120.9(5)
C(17)–C(18)	1.380(8)	C(14)–C(15)–C(16)	120.0(7)
C(18)–C(13)	1.381(7)	C(15)–C(16)–C(17)	119.4(6)
		C(16)–C(17)–C(18)	120.9(5)
		C(17)–C(18)–C(13)	120.2(7)
C(19)–C(20)	1.406(10)	S(1)–C(19)–C(20)	122.9(5)
C(20)–C(21)	1.372(7)	S(1)–C(19)–N(1)	119.7(5)
C(21)–C(22)	1.383(11)	C(20)–C(19)–N(1)	117.4(4)
C(22)–C(23)	1.364(10)	C(19)–C(20)–C(21)	120.1(7)
C(23)–N(1)	1.355(6)	C(20)–C(21)–C(22)	119.8(7)
N(1)–C(19)	1.347(9)	C(21)–C(22)–C(23)	119.9(5)
		C(22)–C(23)–N(1)	119.1(7)
		C(23)–N(1)–C(19)	123.6(6)

(continued)

TABLE 5. *(continued)*

Intramolecular H bridges			
N(1)–HN(1)...Br(1′)	3.308(3)	N(1)–HN(1)...Br(1′)	147
HN(1)–Br(1′)	2.49		
N(1)–HN(1)	0.93		

Transformation for Cu(1′) and S(1′): 1 − *x*, 1 − *y*, 1 − *z*.

TABLE 6. $C_{41}H_{35}NBrP_2SCu$: Interatomic Distances (Å) and Valence Angles (°)

Cu(1)–Br(1)	2.462(2)	Br(1)–Cu(1)–S(1)	114.9(1)
Cu(1)–S(1)	2.302(4)	Br(1)–Cu(1)–P(1)	104.4(1)
Cu(1)–P(1)	2.263(4)	Br(1)–Cu(1)–P(2)	105.9(1)
Cu(1)–P(2)	2.267(4)	S(1)–Cu(1)–P(1)	104.5(2)
		S(1)–Cu(1)–P(2)	102.8(2)
		P(1)–Cu(1)–P(2)	125.0(2)
Br(1)...S(1)	4.017(4)		
Br(1)...P(1)	3.735(4)		
Br(1)...P(2)	3.777(4)		
S(1)...P(1)	3.610(4)		
S(1)...P(2)	3.569(4)		
P(1)...P(2)	4.017(4)		
P(1)–C(1)	1.829(14)	Cu(1)–P(1)–C(1)	115.4(5)
P(1)–C(7)	1.805(15)	Cu(1)–P(1)–C(7)	113.3(5)
P(1)–C(13)	1.805(14)	Cu(1)–P(1)–C(13)	115.0(5)
		C(1)–P(1)–C(7)	102.0(7)
		C(1)–P(1)–C(13)	104.8(8)
		C(7)–P(1)–C(13)	105.0(7)
P(2)–C(19)	1.817(14)	Cu(1)–P(2)–C(19)	113.4(5)
P(2)–C(25)	1.800(15)	Cu(1)–P(2)–C(25)	117.9(5)
P(2)–C(31)	1.810(14)	Cu(1)–P(2)–C(31)	112.6(5)
		C(19)–P(2)–C(25)	103.5(6)
		C(19)–P(2)–C(31)	105.6(6)
		C(25)–P(2)–C(31)	102.6(7)
C(1)–C(2)	1.36(2)	P(1)–C(1)–C(2)	118(1)
C(2)–C(3)	1.39(2)	P(1)–C(1)–C(6)	123(1)
C(3)–C(4)	1.33(2)	C(2)–C(1)–C(6)	119(1)
C(4)–C(5)	1.36(2)	C(1)–C(2)–C(3)	121(1)
C(5)–C(6)	1.40(2)	C(2)–C(3)–C(4)	120(2)
C(6)–C(1)	1.38(2)	C(3)–C(4)–C(5)	121(2)
		C(4)–C(5)–C(6)	119(2)
		C(5)–C(6)–C(1)	120(1)
C(7)–C(8)	1.38(2)	P(1)–C(7)–C(8)	116(1)
C(8)–C(9)	1.39(2)	P(1)–C(7)–C(12)	124(1)
C(9)–C(10)	1.38(2)	C(8)–C(7)–C(12)	120(1)
C(10)–C(11)	1.37(2)	C(7)–C(8)–C(9)	119(1)
C(11)–C(12)	1.39(2)	C(8)–C(9)–C(10)	121(1)
C(12)–C(7)	1.36(2)	C(9)–C(10)–C(11)	119(1)
		C(10)–C(11)–C(12)	120(2)
		C(11)–C(12)–C(7)	121(1)
C(13)–C(14)	1.36(2)	P(1)–C(13)–C(14)	126(1)
C(14)–C(15)	1.37(2)	P(1)–C(13)–C(18)	116(1)
C(15)–C(16)	1.38(2)	C(14)–C(13)–C(18)	118(1)
C(16)–C(17)	1.36(2)	C(13)–C(14)–C(15)	122(1)
C(17)–C(18)	1.38(2)	C(14)–C(15)–C(16)	121(1)
C(18)–C(13)	1.38(2)	C(15)–C(16)–C(17)	117(1)
		C(16)–C(17)–C(18)	122(1)
		C(17)–C(18)–C(13)	120(1)

(continued)

TABLE 6. *(continued)*

C(19)–C(20)	1.43(2)	P(2)–C(19)–C(20)	120(1)
C(20)–C(21)	1.37(2)	P(2)–C(19)–C(24)	119(1)
C(21)–C(22)	1.34(2)	C(20)–C(19)–C(24)	121(1)
C(22)–C(23)	1.39(2)	C(19)–C(20)–C(21)	116(1)
C(23)–C(24)	1.39(2)	C(20)–C(21)–C(22)	123(1)
C(24)–C(19)	1.36(2)	C(21)–C(22)–C(23)	120(1)
		C(22)–C(23)–C(24)	119(1)
		C(23)–C(24)–C(19)	121(1)
C(25)–C(26)	1.38(2)	P(2)–C(25)–C(26)	120(1)
C(26)–C(27)	1.37(2)	P(2)–C(25)–C(30)	122(1)
C(27)–C(28)	1.36(2)	C(26)–C(25)–C(30)	118(1)
C(28)–C(29)	1.39(2)	C(25)–C(26)–C(27)	122(1)
C(29)–C(30)	1.40(2)	C(26)–C(27)–C(28)	120(1)
C(30)–C(25)	1.38(2)	C(27)–C(28)–C(29)	119(1)
		C(28)–C(29)–C(30)	120(1)
		C(29)–C(30)–C(25)	120(1)
C(31)–C(32)	1.39(2)	P(2)–C(31)–C(32)	119(1)
C(32)–C(33)	1.40(2)	P(2)–C(31)–C(36)	122(1)
C(33)–C(34)	1.39(2)	C(32)–C(31)–C(36)	120(1)
C(34)–C(35)	1.37(2)	C(31)–C(32)–C(33)	119(1)
C(35)–C(36)	1.38(2)	C(32)–C(33)–C(34)	122(2)
C(36)–C(31)	1.39(2)	C(33)–C(34)–C(35)	118(2)
		C(34)–C(35)–C(36)	122(2)
		C(35)–C(36)–C(31)	120(1)
S(1)–C(37)	1.69(1)	Cu(1)–S(1)–C(37)	114.7(5)
C(37)–C(38)	1.41(2)	S(1)–C(37)–C(38)	123(1)
C(38)–C(39)	1.34(2)	S(1)–C(37)–N(1)	121(1)
C(39)–C(40)	1.40(2)	C(38)–C(37)–N(1)	116(1)
C(40)–C(41)	1.33(2)	C(37)–C(38)–C(39)	121(1)
C(41)–N(1)	1.34(2)	C(38)–C(39)–C(40)	120(2)
N(1)–C(37)	1.34(2)	C(39)–C(40)–C(41)	119(1)
		C(40)–C(41)–N(1)	121(1)
		C(41)–N(1)–C(37)	123(1)
Intramolecular H bridges			
N(1)–HN(1)...Br(1)	3.31(1)	N(1)–HN(1)–Br(1)	177°
HN(1)...Br(1)	2.39		
N(1)–HN(1)	0.93		

longer than those in $Cu(PPh_3)_2Br$ (Cu–Br = 2.346 Å). The weakened Cu–Br bond can be explained because of short intramolecular Br···H non-bonded contact. The van der Waals radii for H and Br are 1.2 and 1.95 Å respectively. The calculated H···Br distance is 2.49 Å. This H···Br separation is about 0.6 Å shorter than the sum of the relevant van der Waals radii and therefore fulfils Hamilton's criterion [12a] for hydrogen bond formation; comparable literature values are the H···Br separations 2.463 and 2.511 Å in the cyclic $(H_2O\cdot Br^-)_2$ system [12b]. The Cu···Cu′ distance in $[Cu(py2SH)(PPh_3)Br]_2$ (3.420 Å) is comparable to the Cu···Cu′ distance in $[Cu(purinium\text{-}6\text{-}thione)Cl_2]_2$.

Crystal structure of $Cu(py2SH)(PPh_3)_2Br$

The d^{10} metal ion is four-coordinated in what must be described as a distorted tetrahedron. As illustrated in Fig. 2, py2SH acts as a monodentate ligand coordinating through the S atom. The other positions of the tetrahedron are occupied by one bromide atom and two triphenylphosphine ligands. The Cu–S distance is 2.302 Å which is at the lower limit of values reported for $[Cu(py2SH)_4]^+$ (2.278–2.487 Å) [2]. The Cu–P(1) and Cu–P(2) distances of 2.263 and 2.267 Å, respectively, are in good agreement with the distances in the $Cu(PPh_3)_2Br$ complex [13a], but shorter than those in other triphenylphosphine complexes [7, 13b]. The Cu–Br distance of 2.462 Å is consistent with those found in copper(I) compounds [13c], where the Br atom is bound to the metals as a bridge, but longer than that which has been observed previously in the monomer $Cu(PPh_3)_2Br$ complex [13a] (Cu–Br = 2.346 Å). The P–Cu–P angle of 125.0° falls in the middle of the range of values reported for other bis(triphenyl-

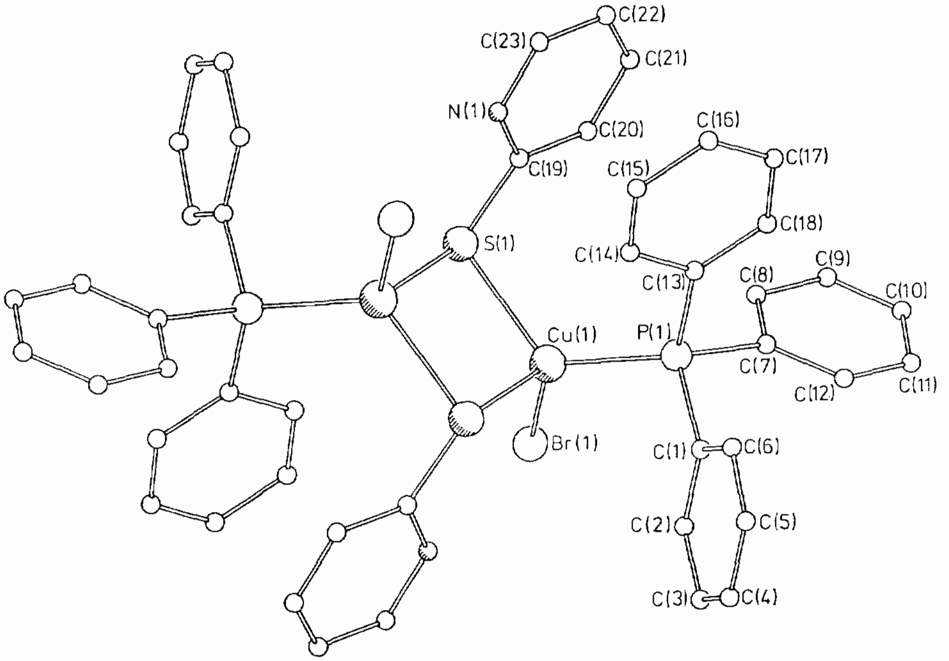


Fig. 1. Structure of [Cu(py2SH)(PPh$_3$)Br]$_2$ with labeling scheme.

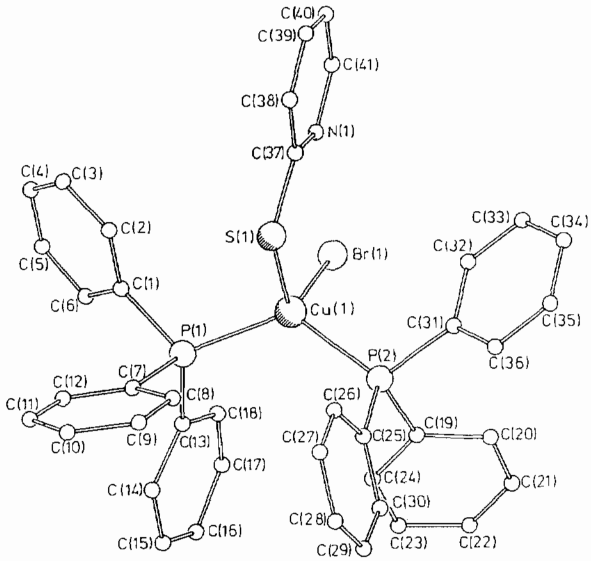
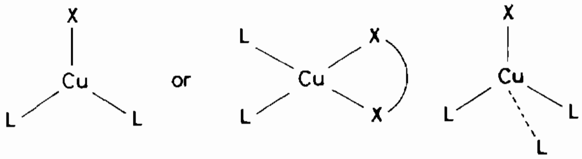


Fig. 2. Structure of Cu(py2SH)(PPh$_3$)$_2$Br with labeling scheme.

phosphine)copper(I) compounds [14–18] such as 126.0° for Cu(PPh$_3$)$_2$Br, 131.2° for Cu(PPh$_3$)$_2$NO$_3$, 123.3° for Cu(PPh$_3$)$_2$BH$_4$, and 125.4° for Cu(bipy)(PPh$_3$)$_2$. This angle is wider than that which has been observed in the complexes [(C$_6$H$_5$)$_2$(CH$_3$)P]$_3$CuCl (108.3°–118.1°), Cu(PPh$_3$)$_3$Cl (109.1°–110.5°) and Cu(py)$_2$(PPh$_3$)$_2$ (115.9°). This is rather surprising because it shows that the P–Cu–P angle is in better agreement with those of planar compounds of general formula **I** rather than with distorted tetrahedra of general formula **II**.

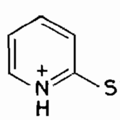


I **II**

Our complex seems to be the first compound to be structurally characterized in the class (PPh$_3$)$_2$CuXX with two different X ligands (Br and S), according to the classification of Lippard *et al.* [7]. The Cu–P–C angles are larger than tetrahedral and the C–P–C angles smaller. This, together with the less-than-tetrahedral values of the P–Cu–S and P–Cu–Br angles (Table 6) compared with the large S–Cu–Br and especially the P–Cu–P angles (see above) reflect the different steric requirements of the ligands in the coordination sphere.

Infrared Spectra

The IR spectra of the complexes show a band at about 3180–3140 cm^{-1} which is assigned to the N–H groups. This N–H band confirms the protonated form of the ligands as well as the coordination of the ligands to the metal through sulfur atoms [19]. For all the ligands the zwitterionic forms **1**, **2**, **3** may favour intramolecular hydrogen bonding and seem to be the predominant forms of bonding [20].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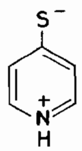
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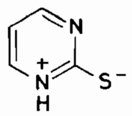
3

NMR Spectra

The ^{1}H NMR spectra of the complexes in $CDCl_3$ solution also provided proof that ligands are protonated. The position (10–14 ppm) and the shape (very broad) of the N–H moiety peaks, indicate the existence of hydrogen bonds. The protonated form of the ligands is also supported by the X-ray data whereby at the site of the N–H proton a small electron density maximum of 0.6 $e^-/Å^3$ was observed in the difference Fourier map.

Electrochemistry

The electrochemical behaviour of the Cu^{I}/Cu^{II} couple for the binuclear complexes was investigated by cyclic voltammetry in acetonitrile (Table 7). The values of E° were measured *versus* the ferrocenium/ferrocene couple as an external redox standard. The redox potentials for the Cu^{I}/Cu^{II} couple were essentially the same for different working-electrode materials (C or Pt) but the reversibility of the electrode processes as judged by peak separation varied as a function of the electrode. A few of the complexes approach nearly reversible electrochemical behaviour as judged by the peak separations (ΔE_p) and current ratio (i_a/i_c) [21] but most of the redox changes must be considered quasireversible by these criteria. Acetonitrile would be expected to make the observed redox potential more positive owing to its well-known ability to stabilize the Cu(I) state. Two oxidative waves and two reductive waves are seen for all the binuclear complexes (Table 7). Given the experimental data presented herein for $Cu^{I}Cu^{I}$, along with the fact that $Zn^{II}Zn^{II}$ has no observable electrochemistry, it is clear that both electrochemical waves found for $Cu^{I}Cu^{I}$ are due to the oxidation of Cu^{I} to Cu^{II} [22].

TABLE 7. Electrochemical Data for the Redox Couple Cu^{II}/Cu^{I} in CH_3CN with 0.1 M Tetraethylammonium perchlorate at 23 ± 2 °C

Compound	E_a (mV)	E_c (mV)	i_a/i_c
$[Cu(py2SH)(PPh_3)Cl]_2$	660	440	0.60
	1070	780	0.70
$[Cu(py2SH)(PPh_3)Br]_2$	590	500	0.65
	750	650	0.62
$[Cu(py2SH)(PPh_3)I]_2$	420	280	0.80
	730	620	0.60
$[Cu(pymtH)(PPh_3)Cl]_2$	450		
	640	410	0.40
	720	650	0.60
$[Cu(pymtH)(PPh_3)Br]_2$	550		
	700	410	0.50
	950	720	0.60
$[Cu(pymtH)(PPh_3)I]_2$	580		
	770	580	0.50
	1080	980	0.45

All of the $E_{1/2}$ values for the mercaptide complexes are in the range of about +0.3 to +1.1 V (*versus* SCE) among the high values reported for the Cu^{I}/Cu^{II} couple [23–25]. This result is in agreement with previous observations that coordination to either mercaptide sulfur or thioether sulfur produces high values for the Cu^{I}/Cu^{II} couple [26–30], an effect which is attributed to the ability of the thioether donor to stabilize the Cu(I) state via a π-acceptor interaction.

Supplementary Material

Tables of additional atomic and thermal parameters for $[Cu(py2SH)(PPh_3)Br]_2$ and $Cu(py2SH)(PPh_3)_2Br$; stereoview packing diagrams; drawings of $C_5H_5NSCuBr$ moiety with H-bridge bond shown; tables of structure factors; cyclic voltammogram of $[Cu(py2SH)(PPh_3)I]_2$; and the ^{1}H NMR spectrum of $[Cu(py2SH)(PPh_3)Br]_2$ are available from the authors on request.

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