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# Binuclear Copper(II) Complexes of Tetradentate (N$_4$) Diazine Ligands. Crystal Structures of [$\mu$-1,4-Bis(4,6-dimethyl-2-pyridylamino)phthalazine-$N$,$\mu$-$N^3$,$\mu$-$N^3$,$N$]-($\mu$-Dichloro)dichlorodicopper(II), [$\mu$-3,6-Bis(2-pyridylthio)pyridazine-$N$,$\mu$-$N^1$,$\mu$-$N^2$,$N$]($\mu$-dichloro)dichlorodicopper(II) ethanol, and 3,6-Bis(2-pyridylthio)pyridazine

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## Abstract

The X-ray structures of two binuclear copper(II) chloride complexes of the tetradentate ligands 1,4-bis(4,6-dimethyl-2-pyridylamino)phthalazine (PAP46-Me) and 3,6-bis(2-pyridylthio)pyridazine are reported. [Cu$_2$(PAP46Me)Cl$_4$] (1) and [Cu$_2$(PTP)Cl$_4$]$\cdot$CH$_3$CH$_2$OH (2) contain triply bridged binuclear centres involving a diazine ($N$–$N$) and two chloro-bridges with copper–copper separations in the range 3.19–3.25 Å and distorted square pyramidal copper stereochemistry. The reduced room temperature magnetic moments indicate antiferromagnetically coupled binuclear copper(II) centres.

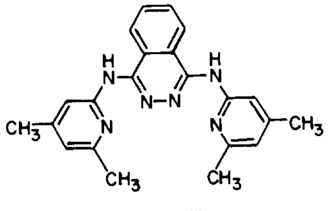
Complex 1 forms green crystals with $a$ = 15.795(3), $b$ = 10.661(3), $c$ = 16.155(4) Å, $\beta$ = 113.82(3)°, $C2/c$, $Z$ = 4, $R_f$ = 0.031. Complex (2) forms green crystals with $a$ = 33.9022(8), $b$ = 9.1626(5), $c$ = 15.7885(5) Å, $\beta$ = 114.853(2)°, $C2/c$, $Z$ = 8, $R_f$ = 0.047. The structure of the ligand PTP is also reported and compared with that of 2.

## Introduction

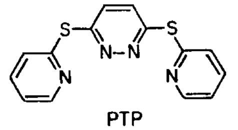
Binuclear copper(II) complexes of tetradentate phthalazine and pyridazine (N$_4$) ligands [1–14] have been found to contain, in most cases, hydroxide bridges, especially when they were synthesized from aqueous solvents. In general these compounds have spin coupled copper centres ($-2J$ = 200–800 cm$^{-1}$) [1, 4, 5, 7] and positive reduction potentials [7–10] involving the passage of two electrons in one apparent reduction step. The structural, magnetic and electrochemical properties of some of these complexes make them particularly attractive as models for the binuclear copper centres found in oxidases and oxygenases (Type III) and in oxyhemocyanins.

While the preferred structural arrangement among these systems involves a hydroxide bridge, in a few cases binuclear copper(II) complexes can be synthesized with just halogen bridges in addition to the diazine bridge. The ligand 3,6-bis(2-pyridyl)-pyridazine (DPPN) reacts with copper salts in aqueous solvents to produce hydroxide bridged compounds but in the presence of acid (HX; X = Cl, Br) tetrahalide complexes e.g. [Cu$_2$(DPPN)Cl$_4$(H$_2$O)]$\cdot$H$_2$O and Cu$_2$(DPPN)Br$_4$, can be produced [15, 16] and an X-ray structure shows that [Cu$_2$(DPPN)Cl$_4$(H$_2$O)]$\cdot$H$_2$O has a chloride bridge [17].

In the present study the complexes [Cu$_2$(PAP46Me)Cl$_4$] (1) and [Cu$_2$(PTP)Cl$_4$]$\cdot$CH$_3$CH$_2$OH (2) were synthesized by reaction of the appropriate ligand with an excess of cupric chloride in aqueous acetonitrile (1) and aqueous methanol (2). An X-ray study on both systems reveals triply bridged binuclear complexes involving two chloro-bridges between the copper(II) centres. An X-ray structure of the ligand PTP is also reported.



PAP46Me



PTP

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## Experimental

Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn Model #7600 Faraday Magnetic Susceptibility System coupled to a Cahn gram electrobalance. C, H, N, and Cl analyses were carried out by Canadian Microanalytical Service, Vancouver.

### *Synthesis of Ligands and Copper Complexes*

The ligands PAP46Me [18] and PTP [10] and the complex $[Cu_2(PAP46Me)Cl_4]$ [7] were synthesized according to published procedures.

#### *$[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (2)*

PTP (0.30 g, 1.0 mmol) was dissolved in boiling ethanol (40 ml) and mixed with a solution of $CuCl_2\cdot 2H_2O$ (0.40 g, 2.3 mmol) in water (40 ml). On heating green crystals formed which were filtered, washed with ethanol and recrystallized from aqueous ethanol. *Anal.* Calc. for $C_{16}H_{16}N_4Cl_4OS_2Cu_2$: C, 31.3; H, 2.61; N, 9.14; Cl, 23.2. Found: C, 31.2; H, 2.60; N, 9.12; Cl, 22.6%.

### *Crystallographic Data Collection and Refinement of the Structures*

#### *$[Cu_2(PAP46Me)Cl_4]$ (1)*

Crystals of **1** are bright green in colour. The diffraction intensities of an approximately 0.10 × 0.13 × 0.30 mm crystal were collected with graphite monochromatized Mo K$\alpha$ radiation by using the $\theta/2\theta$ scan technique with profile analysis [19] to $2\theta_{max} = 40°$ on a Picker four circle diffractometer with a PDP-8e computer. A total of 3065 reflections were measured, of which 2194 were unique, and 1794 reflections were considered to be significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and Polarization factors were applied and no correction was made for absorption. The cell parameters were obtained by the least-squares refinement of the setting angles of 30 reflections with $2\theta > 30°$ ($\lambda$Mo K$\alpha$) = 0.70930 Å). The structure was solved by Patterson and heavy atom techniques and refined by full matrix least squares methods to final residuals of $R_f = 0.031$ and $R_w = 0.018$ for the significant data (0.041 and 0.018 for all data) with unit weights. All hydrogen atoms were located from difference maps. Calculations were performed with the NRC-PDP-8e system of programs [20], adapted for the VAX 11/780 computer. Scattering factors were taken from ref. 21. Crystal data are given in Table I and final atomic positional parameters and equivalent isotropic temperature factors are listed in Table II. See also 'Supplementary Material'.

#### *$[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (2), PTP (3)*

Crystal data collection and the structure solution for **2** and **3** were carried out in a similar manner (intensity data for **2** collected on a Nonius diffractometer using the omega scan mode) and crystal data and other relevant data are summarized in Table I. The ethanol molecule in **2** is highly disordered and has been refined to eight partly occupied non-hydrogen positions. The carbon and oxygen atoms of the ethanol molecule were refined isotropically. All other atoms were refined anisotropically, except H11, H15 and the ethanol hydrogens. H11 and H15 were fixed at calculated positions and included in the last least squares cycle. All hydrogen atoms for **3**, except one, were located from a difference map. Final atomic positional parameters for **2** and **3** are listed in Tables III and IV respectively. See also 'Supplementary Material'.

## Results and Discussion

The pyridylphthalazine ligand PAP46Me reacts with two equivalents of cupric chloride in water/ethanol (6/1) to produce the dark green crystalline compound $[Cu_2(PAP46Me)(OH)Cl_3]\cdot CH_3CH_2OH$, which is characterized by an infrared absorption associated with hydroxide and a very low room temperature magnetic moment ($\mu_{eff}$ = 0.80 BM) [22]. The low magnetic moment suggests strong spin exchange between the copper(II) centres (indicative also of a hydroxide bridge) and is less than that reported for the analogous complex $[Cu_2(PAP6Me)(OH)Cl_3]\cdot 3H_2O$ (PAP6Me = 1,4-bis(6-methyl-2-pyridylamino)phthalazine) ($\mu_{eff}$(RT) = 1.10 BM) for which $-2J = 432$ cm$^{-1}$ [7]. In an attempt to obtain crystalline material of this compound the synthesis was carried out in aqueous acetonitrile ('Experimental'). Suitable crystals for X-ray analysis were obtained but only of the tetrachloro-derivative **1**. The near normal magnetic moment of this system ($\mu_{eff}$(RT) = 1.73 BM) indicates limited spin exchange and the absence of a hydroxide bridge, a feature which is apparent also from the infrared spectrum [7]. The complex $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (**2**), which was synthesized from aqueous ethanol, has a slightly reduced magnetic moment ($\mu_{eff}$(RT) = 1.61 BM) indicating stronger spin exchange between the copper centres. Reaction of PTP with cupric chloride in aqueous methanol in the presence of triethylamine produces the hydroxide bridged complex $[Cu_2(PTP)(OH)Cl_3]$ [23], which has a much lower room temperature moment ($\mu_{eff}$ = 1.43 BM) indicative of moderately strong exchange, typical of systems of this sort [7].

### *Description of the Structures*

The structure of $[Cu_2(PAP46Me)Cl_4]$ (**1**) is shown in Fig. 1. Final atomic positional parameters are given in Table II and bond lengths and bond angles in

TABLE I. Crystal Data

| Compound | [$Cu_2$(PAP46Me)$Cl_4$] (1) | [$Cu_2$(PTP)$Cl_4$]·$CH_3CH_2OH$ (2) | PTP (3) |
|---|---|---|---|
| Formula | $C_{22}H_{22}N_6Cl_4Cu_2$ | $C_{16}H_{16}N_4OS_2Cl_4Cu_2$ | $C_{14}H_{10}N_4S_2$ |
| Formula weight | 639.36 | 613.35 | 298.38 |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | *C2/c* | *C2/c* | *Aa* |
| *a* (Å) | 15.795(3) | 33.9022(8) | 12.033(3) |
| *b* (Å) | 10.661(3) | 9.1626(5) | 5.7756(4) |
| *c* (Å) | 16.155(4) | 15.7885(5) | 18.964(3) |
| α (°) | 90.00 | 90.00 | 90.00 |
| β (°) | 113.82(3) | 114.853(2) | 92.789(20) |
| γ (°) | 90.00 | 90.00 | 90.00 |
| *V* ($Å^3$) | 2488.63 | 4450.22 | 1316.4 |
| *Z* | 4 | 8 | 4 |
| ρ(calc) (g $cm^{-3}$) | 1.706 | 1.831 | 1.506 |
| Crystal size (mm) | 0.10 × 0.13 × 0.30 | 0.4 × 0.15 × 0.04 | 0.4 × 0.35 × 0.25 |
| Crystal colour | green | green | pale yellow |
| Radiation (Å) | Mo Kα (0.70930) | Mo Kα (0.70930) | Mo Kα (0.70930) |
| μ ($mm^{-1}$) | 2.17 | 1.36 | 0.38 |
| 2θ scan range (°) | 49 | 44 | 55 |
| Data collected | 3065 | 4395 | 3898 |
| Unique data | 2194 | 2900 | 2733 |
| With $I > 2.5\sigma(I)$ | 1794 | 2276 | 2565 |
| L.S. parameters | 199 | 292 | 220 |
| Data/parameters | 28 | 44 | 30 |
| $R_f$ (significant data) | 0.031 | 0.047 | 0.028 |
| $R_w$ (significant data) | 0.018 | 0.033 | 0.024 |
| Temp. for data colln. (°) | 22 | 22 | 22 |
| Diffractometer | Picker | Nonius | Picker |

TABLE II. Atomic Positional Parameters (e.s.d.s) for [$Cu_2$(PAP46Me)$Cl_4$] (1)

| Atom | *x* | *y* | *z* | $B_{iso}$ |
|---|---|---|---|---|
| Cu | 0.02643(3) | 0.16971(4) | 0.16262(3) | 2.046(22) |
| Cl1 | −0.10790(6) | 0.23547(8) | 0.16920(6) | 2.91(5) |
| Cl2 | 0.00907(6) | 0.30590(8) | 0.04914(6) | 2.58(5) |
| N1 | 0.13648(17) | 0.09550(24) | 0.14709(18) | 1.87(14) |
| N2 | 0.05601(22) | −0.09629(27) | 0.11082(22) | 2.18(17) |
| N3 | 0.01234(18) | 0.00145(21) | 0.21345(18) | 1.77(15) |
| C1 | 0.12232(22) | −0.0147(3) | 0.10429(22) | 1.75(17) |
| C2 | 0.17096(26) | −0.0525(3) | 0.05320(26) | 2.37(21) |
| C3 | 0.23868(23) | 0.0233(3) | 0.04819(25) | 2.46(20) |
| C4 | 0.25746(26) | 0.1320(4) | 0.09817(27) | 2.81(21) |
| C5 | 0.20793(21) | 0.1671(3) | 0.14732(22) | 2.25(18) |
| C6 | 0.29091(43) | −0.0134(6) | −0.00794(45) | 3.98(32) |
| C7 | 0.23119(34) | 0.2839(4) | 0.20331(37) | 3.56(26) |
| C8 | 0.02666(22) | −0.1044(3) | 0.18037(21) | 1.64(18) |
| C9 | 0.01398(22) | −0.2247(3) | 0.21346(22) | 1.65(17) |
| C10 | 0.02931(27) | −0.3389(4) | 0.18003(24) | 2.50(21) |
| C11 | 0.01452(31) | −0.4489(3) | 0.21486(29) | 3.05(24) |
| H2 | 0.1570(18) | −0.1228(22) | 0.0273(18) | 1.1(7) |
| H4 | 0.3014(16) | 0.1818(23) | 0.1002(18) | 1.0(7) |
| H6A | 0.2570(31) | −0.0519(40) | −0.0616(29) | 8.8(19) |
| H6B | 0.3219(27) | 0.0498(33) | −0.0140(26) | 5.7(14) |
| H6C | 0.3330(30) | −0.0667(38) | 0.0166(30) | 8.2(18) |
| H7A | 0.2796(19) | 0.3262(29) | 0.1965(19) | 3.1(8) |
| H7B | 0.1765(21) | 0.3358(31) | 0.1880(21) | 4.1(10) |
| H7C | 0.2478(24) | 0.2651(35) | 0.2626(22) | 5.5(13) |
| H10 | 0.0496(19) | −0.3391(29) | 0.1369(18) | 2.1(8) |
| H11 | 0.0243(22) | −0.5167(26) | 0.1974(21) | 3.1(9) |
| HN2 | 0.0482(19) | −0.1502(25) | 0.0806(18) | 0.6(8) |

TABLE III. Atomic Positional Parameters (e.s.d.s) for $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (**2**)

| Atom | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| Cu1 | 0.19151(3) | 0.11430(12) | 0.11283(6) | 2.73(6) |
| Cu2 | 0.10870(4) | 0.32396(12) | 0.02456(7) | 3.08(6) |
| Cl1 | 0.21021(8) | −0.02996(25) | 0.02231(14) | 4.08(14) |
| Cl2 | 0.07204(8) | 0.37723(33) | −0.12615(14) | 5.79(17) |
| Cl3 | 0.17419(7) | 0.37421(24) | 0.02437(13) | 3.29(12) |
| Cl4 | 0.12095(7) | 0.04301(23) | 0.04369(14) | 3.68(13) |
| S1 | 0.24372(7) | 0.1111(3) | 0.34491(13) | 3.07(12) |
| S2 | 0.08446(8) | 0.5219(3) | 0.16619(15) | 4.73(15) |
| O1A | 0.0687(6) | 0.1096(19) | 0.7321(10) | 9.9(5) |
| O1B | 0.0848(11) | −0.0441(34) | 0.7646(20) | 11.1(8) |
| N1 | 0.17540(22) | 0.2324(7) | 0.2059(4) | 2.4(4) |
| N2 | 0.14156(20) | 0.3195(8) | 0.1685(4) | 2.5(4) |
| N3 | 0.25359(21) | 0.1740(8) | 0.1879(4) | 2.8(4) |
| N4 | 0.05305(22) | 0.3071(8) | 0.0393(5) | 3.2(4) |
| C1A | 0.0498(18) | −0.0300(61) | 0.7242(31) | 10.6(14) |
| C1B | 0.0612(11) | −0.1124(38) | 0.7930(24) | 8.6(8) |
| C1C | 0.0611(19) | −0.0034(65) | 0.8009(36) | 11.7(16) |
| C2A | 0.0351(16) | 0.0847(64) | 0.7313(37) | 12.1(17) |
| C2B | 0.0953(18) | −0.1334(48) | 0.8337(28) | 8.8(12) |
| C2C | 0.1142(11) | −0.0528(43) | 0.8218(27) | 9.1(11) |
| C3 | 0.1292(3) | 0.4026(10) | 0.2229(5) | 3.2(5) |
| C4 | 0.1526(3) | 0.4040(10) | 0.3198(5) | 3.2(5) |
| C5 | 0.1876(3) | 0.3196(10) | 0.3585(5) | 2.8(5) |
| C6 | 0.1996(3) | 0.2313(9) | 0.2994(5) | 2.6(5) |
| C7 | 0.2737(3) | 0.1811(9) | 0.2834(5) | 2.5(5) |
| C8 | 0.3146(3) | 0.2251(10) | 0.3328(6) | 3.1(5) |
| C9 | 0.3383(3) | 0.2733(10) | 0.2849(7) | 3.4(6) |
| C10 | 0.3183(3) | 0.2701(10) | 0.1878(6) | 4.2(6) |
| C11 | 0.2762(3) | 0.2224(10) | 0.1442(5) | 3.5(6) |
| C12 | 0.0450(3) | 0.3936(11) | 0.0996(6) | 3.4(6) |
| C13 | 0.0059(4) | 0.3901(15) | 0.1073(8) | 5.1(8) |
| C14 | −0.0272(4) | 0.2981(15) | 0.0518(9) | 5.8(8) |
| C15 | −0.0175(4) | 0.2087(14) | −0.0064(9) | 5.9(8) |
| C16 | 0.0222(3) | 0.2148(11) | −0.0129(7) | 4.5(6) |
| H4 | 0.1429(17) | 0.454(6) | 0.347(3) | 3.2(13) |
| H5 | 0.2065(23) | 0.318(8) | 0.433(5) | 5.2(23) |
| H8 | 0.3324(20) | 0.225(7) | 0.400(4) | 2.6(18) |
| H9 | 0.3674(22) | 0.288(8) | 0.314(5) | 3.4(22) |
| H10 | 0.3303(20) | 0.312(7) | 0.164(4) | 3.2(17) |
| H11 | 0.2614(0) | 0.221(0) | 0.066(0) | 4.2(0) |
| H13 | 0.0043(32) | 0.457(9) | 0.143(6) | 5.4(33) |
| H14 | −0.0602(32) | 0.319(12) | 0.059(6) | 11.5(38) |
| H15 | −0.0375(22) | 0.157(8) | −0.045(5) | 3.0(24) |
| H16 | 0.0285(0) | 0.141(0) | −0.061(0) | 5.2(0) |

Table V. The two copper centres are bound in a triple bridged arrangement involving two chloro-bridges and a phthalazine diazine bridge. The angle at the chlorine bridges is 83.57° with a copper–copper separation of 3.251 Å. This copper–copper distance is significantly longer than that found for the analogous hydroxide-bridged complex $[Cu_2(PAP6Me)(OH)Cl_3]\cdot 3H_2O$ (3.137 Å) and can be attributed to the presence of two more bulky chlorine bridges in **1**. The stereochemistry at each copper atom can be best described as a distorted square pyramid in which the copper is displaced by 0.293 Å from the mean plane of the basal donor set (N(1), N(3), Cl(2), Cl(1)). The ligand itself is twisted with angles of 35.7° and 36.3° respectively between pyridine rings 1 and 2 and the mean plane of the flat phthalazine entity (3) (Fig. 1). The mean planes of rings 1 and 2 are mutually inclined by 55.7° in keeping with the two-fold symmetry axis which bisects the molecule. The ligand adopts a molecular twist which is unusual among complexes of this sort containing hydroxide bridges, in which the disposition of the two peripheral

TABLE IV. Atomic Positional Parameters (e.s.d.s) for PTP

| Atom | *x* | *y* | *z* | $B_{iso}$ |
|---|---|---|---|---|
| S1 | 1.01739(0) | 0.14838(13) | 0.43236(0) | 3.89(3) |
| S2 | 0.74511(5) | 0.85444(13) | 0.59562(3) | 3.85(3) |
| N1 | 1.20817(18) | 0.1813(4) | 0.37755(11) | 3.14(8) |
| N2 | 0.97741(17) | 0.5504(4) | 0.49706(12) | 3.03(8) |
| N3 | 0.91617(18) | 0.6953(4) | 0.53380(11) | 3.08(8) |
| N4 | 0.66332(18) | 0.5000(4) | 0.66755(12) | 2.93(8) |
| C1 | 1.11679(21) | 0.3082(5) | 0.38639(12) | 2.53(10) |
| C2 | 1.10178(24) | 0.5287(5) | 0.35907(15) | 3.11(10) |
| C3 | 1.18365(26) | 0.6207(5) | 0.32009(13) | 3.32(12) |
| C4 | 1.27910(27) | 0.4914(6) | 0.31024(17) | 3.79(12) |
| C5 | 1.28574(24) | 0.2755(5) | 0.33920(16) | 3.61(11) |
| C6 | 0.93260(21) | 0.3539(5) | 0.47322(12) | 2.60(9) |
| C7 | 0.82306(20) | 0.2912(5) | 0.48236(12) | 2.53(9) |
| C8 | 0.75977(19) | 0.4374(5) | 0.52164(13) | 2.62(9) |
| C9 | 0.81179(21) | 0.6382(5) | 0.54685(12) | 2.66(10) |
| C10 | 0.63729(20) | 0.7013(5) | 0.63616(13) | 2.57(10) |
| C11 | 0.53403(21) | 0.8014(5) | 0.63656(13) | 2.91(10) |
| C12 | 0.45247(23) | 0.6920(6) | 0.67239(15) | 3.63(11) |
| C13 | 0.47701(27) | 0.4833(6) | 0.70424(17) | 3.76(11) |
| C14 | 0.58168(28) | 0.3948(5) | 0.69990(14) | 3.41(12) |
| H2 | 1.0363(14) | 0.600(3) | 0.3680(9) | 3.0(4) |
| H3 | 1.1758(24) | 0.775(6) | 0.2992(14) | 6.0(8) |
| H4 | 1.3342(24) | 0.548(4) | 0.2831(13) | 4.5(6) |
| H5 | 1.3479(19) | 0.186(4) | 0.3320(13) | 5.2(6) |
| H7 | 0.7960(14) | 0.174(3) | 0.4641(9) | 2.5(4) |
| H8 | 0.6850(15) | 0.416(3) | 0.5281(9) | 3.3(4) |
| H11 | 0.5212(14) | 0.932(3) | 0.6119(9) | 2.7(4) |
| H12 | 0.3786(19) | 0.760(4) | 0.6747(10) | 4.2(5) |
| H13 | 0.4167(25) | 0.399(5) | 0.7274(15) | 6.3(8) |
| H14 | 0.5981(16) | 0.248(5) | 0.7223(10) | 2.5(5) |

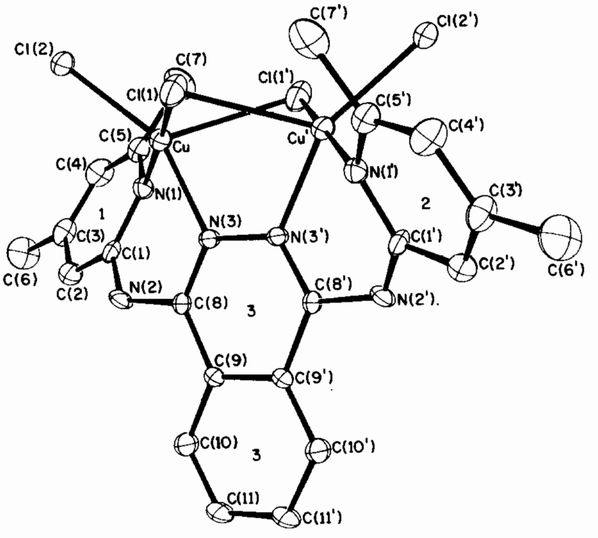

Fig. 1. Structural representation for [$Cu_2$(PAP46Me)$Cl_4$] (**1**) with hydrogen atoms omitted (40% ellipsoids).

TABLE V. Selected Bond Distance (Å) and Angles (°) (e.s.d.s) for [$Cu_2$(PAP46Me)$Cl_4$] (**1**)

| | | | |
|---|---|---|---|
| Cu–Cu′ | 3.251(1) | C(9)–C(10) | 1.392(5) |
| Cu–Cl(1) | 2.277(1) | C(10)–C(11) | 1.362(5) |
| Cu–Cl(1) | 2.589(1) | C(11)–C(11′) | 1.386(7) |
| Cu–Cl(2) | 2.267(1) | C(9)–C(9′) | 1.418(6) |
| Cu–N(1) | 2.016(2) | Cu–Cl(1)–Cu′ | 83.57(4) |
| Cu–N(3) | 2.022(2) | Cl(2)–Cu–N(3) | 154.08(8) |
| N(1)–C(5) | 1.361(4) | Cl(1)–Cu–N(1) | 173.30(8) |
| C(5)–C(7) | 1.495(6) | N(3)–Cu–Cl(1) | 89.81(8) |
| C(5)–C(4) | 1.373(5) | Cl(1)–Cu–Cl(2) | 91.72(4) |
| C(4)–C(3) | 1.375(6) | Cl(2)–Cu–N(1) | 88.82(8) |
| C(3)–C(6) | 1.504(6) | N(1)–Cu–N(3) | 86.8(1) |
| C(3)–C(2) | 1.369(5) | Cl(1)–Cu–Cl(1′) | 86.86(4) |
| C(2)–C(1) | 1.395(5) | Cl(1′)–Cu–Cl(2) | 121.45(4) |
| C(1)–N(1) | 1.335(4) | Cl(1′)–Cu–N(1) | 98.55(8) |
| C(1)–N(2) | 1.398(4) | Cl(1′)–Cu–N(3) | 84.47(8) |
| N(2)–C(8) | 1.380(4) | C(1)–N(2)–C(8) | 127.5(3) |
| C(8)–N(3) | 1.307(4) | | |
| N(3)–N(3′) | 1.385(5) | | |
| C(8)–C(9) | 1.435(4) | | |

pyridine rings and the central phthalazine moiety resembles the claws and body of a lobster, involving planar symmetry requirements [1–9]. The different ligand conformation also results in a different disposition of the two copper square pyramids in **1**. Whereas in most of the hydroxide bridged species both copper

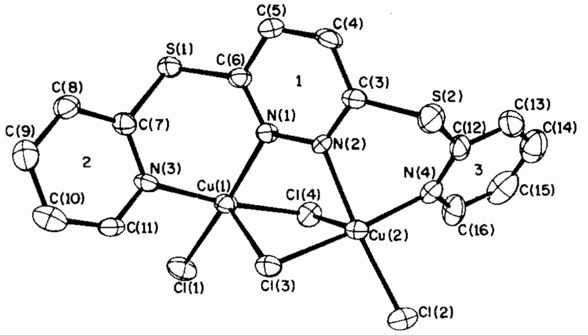

Fig. 2. Structural representation for $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (**2**) with the disordered ethanol molecule and hydrogen atoms omitted (40% ellipsoids).

TABLE VI. Selected Bond Distances (Å) and Angles (°) (e.s.d.s) for $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (**2**)

| | | | |
|---|---|---|---|
| Cu(1)–Cu(2) | 3.198(1) | C(8)–C(9) | 1.386(15) |
| Cu(1)–N(1) | 2.075(6) | C(9)–C(10) | 1.392(13) |
| Cu(1)–N(3) | 2.009(6) | C(10)–C(11) | 1.368(13) |
| Cu(1)–Cl(1) | 2.226(2) | C(11)–N(3) | 1.307(11) |
| Cu(1)–Cl(3) | 2.698(2) | N(3)–C(7) | 1.370(10) |
| Cu(1)–Cl(4) | 2.268(2) | Cu(1)–Cl(3)–Cu(2) | 79.65(7) |
| Cu(2)–N(2) | 2.069(5) | Cu(1)–Cl(4)–Cu(2) | 81.70(8) |
| Cu(2)–N(4) | 2.002(7) | N(1)–Cu(1)–Cl(1) | 174.6(2) |
| Cu(2)–Cl(2) | 2.227(2) | N(3)–Cu(1)–Cl(4) | 173.5(2) |
| Cu(2)–Cl(3) | 2.269(2) | N(1)–Cu(1)–N(3) | 87.8(3) |
| Cu(2)–Cl(4) | 2.605(2) | N(3)–Cu(1)–Cl(1) | 91.7(2) |
| N(4)–C(16) | 1.327(13) | Cl(1)–Cu(1)–Cl(4) | 92.7(1) |
| C(16)–C(15) | 1.396(18) | Cl(4)–Cu(1)–N(1) | 87.3(2) |
| C(15)–C(14) | 1.371(22) | Cl(1)–Cu(1)–Cl(3) | 104.5(1) |
| C(14)–C(13) | 1.383(21) | N(3)–Cu(1)–Cl(3) | 90.6(2) |
| C(13)–C(12) | 1.383(16) | N(1)–Cu(1)–Cl(3) | 80.9(2) |
| C(12)–S(2) | 1.758(9) | Cl(4)–Cu(1)–Cl(3) | 92.8(1) |
| C(12)–N(4) | 1.351(13) | N(2)–Cu(2)–Cl(2) | 168.3(2) |
| S(2)–C(3) | 1.777(8) | N(4)–Cu(2)–Cl(3) | 170.6(2) |
| N(1)–N(2) | 1.316(9) | N(2)–Cu(2)–Cl(3) | 86.0(2) |
| N(2)–C(3) | 1.339(11) | Cl(3)–Cu(2)–Cl(2) | 93.5(1) |
| C(3)–C(4) | 1.396(10) | Cl(2)–Cu(2)–N(4) | 90.6(2) |
| C(4)–C(5) | 1.331(12) | N(4)–Cu(2)–N(2) | 88.2(3) |
| C(5)–C(6) | 1.418(12) | N(2)–Cu(2)–Cl(4) | 82.4(2) |
| C(6)–N(1) | 1.354(9) | Cl(3)–Cu(2)–Cl(4) | 95.3(1) |
| C(6)–S(1) | 1.749(8) | Cl(2)–Cu(2)–Cl(4) | 109.3(1) |
| S(1)–C(7) | 1.794(8) | N(4)–Cu(2)–Cl(4) | 91.3(2) |
| C(7)–C(8) | 1.335(12) | C(3)–S(2)–Cl(2) | 99.4(4) |
| | | C(7)–S(1)–C(6) | 97.7(4) |

atoms are bridged at hydroxide by an equatorial interaction, the chlorine bridges in **1** each involve an equatorial and axial interaction to each copper centre. The equatorial copper–chlorine bridge bond length is relatively short (2.277 Å) whereas a somewhat longer axial copper–chlorine bridge separation (2.589 Å) exists. Other copper–ligand bond distances are typical for systems of this sort.

The structure of $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (**2**) is shown in Fig. 2. Final atomic positional parameters are given in Table III and bond lengths and bond angles in Table VI. The structure of the ligand itself is shown in Fig. 3 and final atomic positional parameters and bond lengths and bond angles are given in Tables IV and VII respectively. The two square pyramidal copper centres in **2** are bridged by two chlorine atoms and the pyridazine nitrogen pair with chlorine bridge angles of 79.65° and 81.70° and a copper–copper separation of 3.198 Å. This copper–copper distance is somewhat shorter than that observed in **1** and can be attributed, in part, to the absence of a 6-methyl residue on the pyridine rings, a feature which caused dramatic changes in the dimensions of the binuclear copper centres in complexes of pyridylaminophthalazine ligands [5, 7, 8]. However, this comparison must take into account other features of the ligands, namely the angle at the exocyclic bridge position and also the associated bond lengths. In the free ligand, PTP, carbon–sulfur bond lengths fall within the range 1.76–1.78 Å with angles C(1)–S(1)–C(6) and C(9)–S(2)–C(10) of 106.5° and 103.5° respectively. Comparable carbon–sulfur bond lengths are found in **2** but the sulfur bridge angles are somewhat smaller (97.9°, 99.4°). In comparing the complexes **1** and **2** the larger apparent ligand bite of the ligand PTP associated with the long carbon–sulfur linkages has been

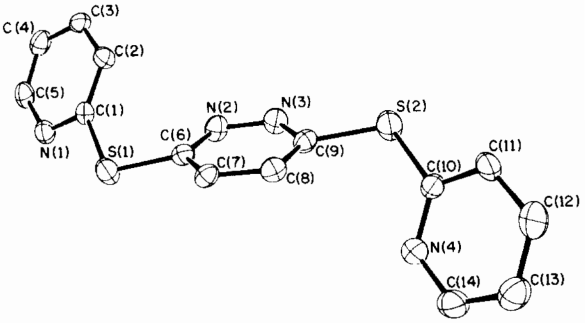

Fig. 3. Structural representation for the ligand PTP with hydrogen atoms omitted (40% ellipsoids).

TABLE VII. Selected Bond Distance (Å) and Angles (°) (e.s.d.s) for PTP (**3**)

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1.384(4) | N(3)–N(2) | 1.334(3) |
| C(2)–C(3) | 1.367(4) | N(2)–C(6) | 1.326(4) |
| C(3)–C(4) | 1.390(5) | C(9)–S(2) | 1.770(3) |
| C(4)–C(5) | 1.363(5) | S(2)–C(10) | 1.776(3) |
| C(5)–N(1) | 1.328(4) | C(10)–C(11) | 1.371(4) |
| N(1)–C(1) | 1.339(3) | C(11)–C(12) | 1.374(4) |
| C(1)–S(1) | 1.773(3) | C(12)–C(13) | 1.374(5) |
| S(1)–C(6) | 1.768(3) | C(13)–C(14) | 1.365(5) |
| C(6)–C(7) | 1.386(4) | C(14)–N(4) | 1.330(4) |
| C(7)–C(8) | 1.379(4) | N(4)–C(10) | 1.336(3) |
| C(8)–C(9) | 1.392(4) | C(1)–S(1)–C(6) | 106.5(1) |
| C(9)–N(3) | 1.333(3) | C(10–S(2)–C(9) | 103.5(1) |

partly offset by the smaller angle at the sulfur bridge. For **1** the exocyclic carbon–nitrogen bond lengths are significantly shorter (1.38–1.40 Å) while the angle at the exocyclic nitrogen atom is much larger (127.5°).

The ligand in **2** is severely twisted with angles of 116.1° and 121.7° respectively between pyridine rings 2 and 3 and the pyridazine plane (1) and an angle of 46.8° between the two pyridine planes (Fig. 2). Cu(1) is displaced by 0.092 Å above the mean plane of the atoms Cl(1), Cl(4), N(1), N(3) while for Cu(2) a much larger equivalent displacement (0.186 Å) exists. The unsymmetrical, twisted nature of the ligand is comparable with that found in **1**. Also a similar situation involving the chlorine bridge bond lengths exists in both compounds. Each chlorine bridge forms both an axial and an equatorial interaction with the copper centres in **2** leading to one long copper–chlorine bond (2.60–2.70 Å) and one short bond (2.22–2.27 Å).

The asymmetric nature of the chlorine bridging network in both **1** and **2** leads to an interesting situation with respect to the magnetic properties of these systems. The symmetric square pyramidal binuclear copper(II) complexes of the pyridylaminophthalazine ligands, which involve in plane bonding to a hydroxide bridge, exhibit significant antiferromagnetic exchange between the copper centres, the magnitude of which varies in a linear fashion as a function of hydroxide bridge angle within the series [5, 7]. In these systems the magnetic exchange interaction is assumed to occur largely through overlap of the 'magnetic', $d_{x^2-y^2}$, orbitals with an oxygen p orbital. The diazine bridge is considered to provide a small contribution to the total exchange in these systems. In the case of **1** and **2** the asymmetric nature of the binuclear centres effectively generates a situation where magnetic exchange via the chlorine bridges is unlikely. This results because only one copper orbital per chlorine bridge is a 'magnetic' orbital. Spin exchange can however occur via the diazine bridge, which is bonded to the $d_{x^2-y^2}$ orbital of both copper centres. The reduced room temperature magnetic moments for **1** and **2** (1.73 and 1.61 BM respectively) indicate that spin exchange does exist between the copper(II) centres.

In the absence of a variable temperature magnetic study on these systems an estimate of the magnitude of the exchange integral can be obtained by substituting into the Van Vleck equation, as has been demonstrated recently [24]. Assuming a $g$ value of 2.1 and a temperature of 296 K estimates of $-2J$ of 70 and 150 $cm^{-1}$ are obtained for **1** and **2** respectively. Clearly, therefore, the diazine bridge does mediate spin exchange between the copper centres and it appears that a pyridazine bridge is more effective than phthalazine.

## Supplementary Material

Anisotropic thermal parameters and a listing of structure factors for all compounds are available as supplementary material.

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## References

1 L. K. Thompson, V. T. Chacko, J. A. Elvidge, A. B. P. Lever and R. V. Parish, *Can. J. Chem., 47,* 4141 (1969).
2 G. Marongiu and E. C. Lingafelter, *Acta Crystallogr., Sect. B, 38,* 620 (1982).
3 L. K. Thompson, *Can. J. Chem., 61,* 579 (1983).
4 L. K. Thompson, F. W. Hartstock, P. Robichaud and A. W. Hanson, *Can. J. Chem., 62,* 2755 (1984).
5 L. K. Thompson, A. W. Hanson and B. S. Ramaswamy, *Inorg. Chem., 23,* 2459 (1984).
6 L. K. Thompson, T. C. Woon, D. B. Murphy, E. J. Gabe, F. L. Lee and Y. LePage, *Inorg. Chem., 24,* 4719 (1985).
7 S. K. Mandal, T. C. Woon, L. K. Thompson, M. J. Newlands and E. J. Gabe, *Aust. J. Chem., 39,* 1007 (1986).
8 S. K. Mandal, L. K. Thompson and A. W. Hanson, *J. Chem. Soc., Chem. Comm.,* 1709 (1985).
9 L. K. Thompson, S. K. Mandal, E. J. Gabe, F. L. Lee and A. W. Addison, *Inorg. Chem.,* in press.
10 T. C. Woon, R. McDonald, S. K. Mandal, L. K. Thompson and A. W. Addison, *J. Chem. Soc., Dalton Trans.,* in press.
11 M. Ghedini, G. De Munno, G. Denti, A. M. Manotti Lanfredi and A. Tiripicchio, *Inorg. Chim. Acta, 57,* 87 (1982).
12 P. Dapporto, G. De Munno, G. Bruno and M. Romeo, *Acta Crystallogr., Sect. C, 39,* 718 (1983).
13 G. De Munno and G. Denti, *Acta Crystallogr., Sect. C, 40,* 616 (1984).
14 P. Dapporto, G. De Munno, A. Sega and C. Mealli, *Inorg. Chim. Acta, 83,* 171 (1984).
15 D. Dapporto, G. De Munno, A. Sega and C. Mealli, *Inorg. Chim. Acta, 83,* 171 (1984).
16 G. De Munno, G. Denti and P. Dapporto, *Inorg. Chim. Acta, 74,* 199 (1983).
17 G. De Munno and G. Bruno, *Acta Crystallogr., Sect. C, 40,* 2022 (1984).
18 D. V. Bautista, G. Bullock, F. W. Hartstock and L. K. Thompson, *J. Heterocyclic Chem., 20,* 345 (1983).
19 D. F. Grant and E. J. Gabe, *J. Appl. Crystallogr., 11,* 114 (1978).
20 A. C. Larson and E. J. Gabe, 'Computing in Crystallography', Delft University Press, Delft, Holland, 1978, p. 81.
21 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1974, Table 2.2B, p. 99.
22 G. Bullock, F. W. Hartstock and L. K. Thompson, *Can. J. Chem., 61,* 57 (1983).
23 S. K. Mandal and L. K. Thompson, unpublished observations.
24 L. K. Thompson and B. S. Ramaswamy, *Inorg. Chem., 25,* 2664 (1986).