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Dinuclear and Tetranuclear Copper(II) Complexes of the Tetradentate Ligand 1,4-Bis(2-pyridylthio)phthalazine: Structural, Magnetic, and Electrochemical Studies

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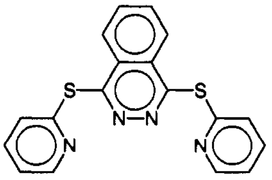
The tetradentate ligand 1,4-bis(2-pyridylthio)phthalazine (PTPH) forms dinuclear copper(II) complexes $[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$ (**1**) and $[Cu_2(PTPH)Br_4]\cdot 1.5H_2O$ (**2**), involving both diazine and double halogen bridges between the copper centers, an unusual tetranuclear complex $[Cu_2(PTPH)(\mu_3\text{-}OH)(NO_3)_3(H_2O)]_2$ (**3**), and a dinuclear nitrate complex $[Cu_2(PTPH)(\mu_2\text{-}OH)(NO_3)_2(H_2O)_2](NO_3)$ (**4**). **1** crystallizes in the monoclinic system, space group $C2/c$, with a = 20.710(4) Å, b = 11.694(3) Å, c = 15.509(4) Å, β = 133.85(1)°, and Z = 8. **3** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 12.075(2) Å, b = 12.344(1) Å, c = 8.728(2) Å, α = 97.78(1)°, β = 96.70(1)°, γ = 110.390(9)°, and Z = 2. **4** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 10.687(3) Å, b = 13.472(3) Å, c = 9.638(2) Å, α = 103.03(2)°, β = 90.75(2)°, γ = 110.44(2)°, and Z = 2. Variable-temperature magnetic measurements for **1**–**4** show dominant antiferromagnetic coupling with $-2J$ values in the range 124–313 cm^{-1}. A significant pyramidal distortion at the μ_3-OH in **3** suppresses the antiferromagnetic exchange below the anticipated value. Compounds **1** and **2** exhibit two-electron reduction at positive potentials (vs SCE), to produce rearranged dinuclear copper(I) species.

Introduction

Tetradentate (N_4) phthalazines and pyridazines have received a great deal of attention in recent years, as primary examples of ligands that, as a result of possessing a heteroaromatic 1,2-diazine fragment, preferentially bind two metals in close proximity.[1-27] These ligands have created an ideal framework for several magneto–structural studies involving dicopper(II) complexes, in which structural parameters, e.g. the hydroxide bridge angle (Cu–O(H)–Cu), have been varied over a very wide range (100–126°), by the selective use of ligand constraints, e.g. variable chelate ring size, and steric constraints. In a series of complexes with an "essentially constant" dinuclear center involving the two copper atoms and the diazine group, with $d_{x^2-y^2}$ ground-state copper ions, a reasonable linear relationship was observed between exchange integral ($-2J$) and the Cu–O(H)–Cu bridge angle,[21] a study which complemented the earlier, classical study of Hatfield and coworkers on dihydroxy-bridged dicopper(II) complexes.[28]

The principal focus of the earlier work concerned (pyridylamino)phthalazine ligands (PAPR), which involved secondary amine linkages between the diazine ring and the peripheral pyridines. Comparable N_4 (pyridylamino)pyridazine ligands were not synthesized, but a series of ligands derived by reaction of 3,6-dichloropyridazine with thiols, which involved a thioether linkage between the diazine ring and the peripheral donor groups,[29-32] were investigated. Little attention was focused on corresponding thioether ligands derived from 1,4-dichlorophthalazine, except for the complex $[Cu_2(PTPH)(OH)Cl_3]\cdot MeOH\cdot H_2O$ (PTPH = 1,4-bis(2-pyridylthio)phthalazine,[29] for which no structural details are available.



PTPH

The present study involves the synthesis and study of several other dinuclear complexes of PTPH and a most unusual

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(1) Thompson, L. K.; Chacko, V. T.; Elvidge, J. A.; Lever, A. B. P.; Parish, R. V. *Can. J. Chem.* **1969**, *47*, 4141.
(2) Andrew, J. E.; Ball, P. W.; Blake, A. B. *J. Chem. Soc., Chem. Commun.* **1969**, 143.
(3) Andrew, J. E.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1408.
(4) Ball, P. W.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1415.
(5) Lever, A. B. P.; Thompson, L. K.; Reiff, W. M. *Inorg. Chem.* **1972**, *11*, 104.
(6) Ball, P. W.; Blake, A. B. *J. Chem. Soc., Dalton Trans.* **1974**, 852.
(7) Ghedini, M.; De Munno, G.; Denti, G.; Manotti Lanfredi, A. M.; Tiripicchio, A. *Inorg. Chim. Acta* **1982**, *57*, 87.
(8) Banci, L.; Bencini, A.; Benelli, C.; Gatteschi, D. *Inorg. Chem.* **1982**, *21*, 3868.
(9) Dapporto, P.; De Munno, G.; Bruno, G.; Romeo, M. *Acta Crystallogr.* **1983**, *C39*, 718.
(10) Tiripicchio, A.; Manotti Lanfredi, A. M.; Ghedini, M.; Neve, F. *J. Chem. Soc., Chem. Commun.* **1983**, 97.
(11) De Munno, G.; Denti, G.; Dapporto, P. *Inorg. Chim. Acta* **1983**, *74*, 199.
(12) De Munno, G.; Denti, G. *Acta Crystallogr.* **1984**, *C40*, 616.
(13) De Munno, G.; Bruno, G. *Acta Crystallogr.* **1984**, *C40*, 2022.
(14) Dapporto, P.; De Munno, G.; Sega, A.; Mealli, C. *Inorg. Chim. Acta* **1984**, *83*, 171.
(15) Ghedini, M.; Neve, F.; Morazzoni, F.; Oliva, C. *Polyhedron* **1985**, *4*, 497.
(16) Attanasio, D.; Dessy, G.; Fares, V. *Inorg. Chim. Acta* **1985**, *104*, 99.
(17) Attanasio, D.; Fares, V.; Imperatori, P. *J. Chem. Soc., Chem. Commun.* **1986**, 1476.
(18) Drew, M. G. B.; Yates, P. C.; Trocha-Grimshaw, J.; Lavery, A.; McKillop, K. P.; Nelson, S. M.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1988**, 347.
(19) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Rubio Gonzalez, J. M.; Garcia-Granda, S. *Polyhedron* **1990**, *9*, 2603.
(20) Abraham, F.; Lagrenee, M.; Sueur, S.; Mernari, B.; Bremard, C. *J. Chem. Soc., Dalton Trans.* **1991**, 1443.
(21) Thompson, L. K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1988**, *27*, 39.
(22) Thompson, L. K.; Mandal, S. K.; Charland, J.-P.; Gabe, E. J. *Can. J. Chem.* **1988**, *66*, 348.
(23) Wen, T.; Thompson, L. K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1988**, *27*, 4190.
(24) Mandal, S. K.; Thompson, L. K.; Gabe, E. J.; Charland, J.-P.; Lee, F. L. *Inorg. Chem.* **1988**, *27*, 855.
(25) Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Charland, J.-P.; Gabe, E. J. *Inorg. Chim. Acta* **1990**, *178*, 169.
(26) Lacroix, P.; Kahn, O.; Valade, L.; Cassoux, P.; Thompson, L. K. *Synth. Met.* **1990**, *39*, 81.
(27) Tandon, S. S.; Thompson, L. K.; Hynes, R. C. *Inorg. Chem.* **1992**, *31*, 2210.
(28) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.
(29) Woon, T. C.; McDonald, R.; Mandal, S. K.; Thompson, L. K.; Connors, S. P.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1986**, 2381.
(30) Mandal, S. K.; Thompson, L. K.; Newlands, M. J.; Lee, F. L.; Le Page, Y.; Charland, J.-P.; Gabe, E. J. *Inorg. Chim. Acta* **1986**, *122*, 199.
(31) Mandal, S. K.; Thompson, L. K.; Gabe, E. J.; Lee, F. L.; Charland, J.-P. *Inorg. Chem.* **1987**, *26*, 2384.
(32) Thompson, L. K.; Mandal, S. K.; Rosenberg, L.; Lee, F. L.; Gabe, E. J. *Inorg. Chim. Acta* **1987**, *133*, 81.

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tetranuclear copper(II) complex. With copper(II) nitrate, two radically different complexes are produced depending on very subtle differences in reaction conditions. A dinuclear species, typical of complexes of this sort, with a μ_2-hydroxide and a μ_2-diazine bridge and a tetranuclear complex involving μ_2-diazine and μ_3-hydroxide bridges are produced. The variable-temperature magnetic properties and electrochemical properties of these complexes will be discussed in relation to their structures and those of related systems.

Experimental Section

Synthesis of Complexes. $[Cu_2(PTPH)Cl_4]\cdot 2H_2O$ (1). PTPH[29] (0.35 g, 1.0 mmol) was dissolved in boiling MeOH (40 mL) and a solution of 0.35 g of $CuCl_2\cdot 2H_2O$ (2.0 mmol) in 10 mL of H_2O added. The resulting mixture was allowed to stir at room temperature for 2 h. Green crystals formed, which were filtered off, washed with methanol, and dried under vacuum. Yield: 70%. Anal. Calcd for $C_{18}H_{20}N_4Cl_4O_2S_2Cu_2$: C, 33.09; H, 2.47; N, 8.57. Found: C, 33.15; H, 2.25; N, 8.22. The crystals for X-ray diffraction were obtained by diffusing diethyl ether into a methanol solution of the complex and have the formula $[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$.

$[Cu_2(PTPH)Br_4]\cdot 1.5H_2O$ (2) was prepared in a similar manner using $CuBr_2$ and was obtained as brown crystals. Anal. Calcd for $C_{18}H_{15}N_4Br_4O_{1.5}S_2Cu_2$: C, 26.30; H, 1.84; N, 6.82. Found: C, 26.15; H, 1.61; N, 7.20.

$[Cu_2(PTPH)(OH)(NO_3)_3(H_2O)]_2$ (3). PTPH (0.35 g, 1.0 mmol) was dissolved in $CHCl_3$ (5 mL) and a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.48 g, 2.0 mmol) in 30 mL of CH_3CN added. The light blue solution was kept at room temperature overnight. Light blue crystals formed, which were filtered off, washed with acetonitrile, and dried under vacuum. Yield: 90%. Anal. Calcd for $C_{18}H_{15}O_{11}N_7S_2Cu_2$: C, 31.04; H, 2.17; N, 14.08. Found: C, 31.36; H, 2.22; N, 14.44.

$[Cu_2(PTPH)(OH)(NO_3)_2(H_2O)_2](NO_3)$ (4). PTPH (0.35 g, 1.0 mmol) was dissolved in $CHCl_3$ (5 mL), and a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.48 g, 2.0 mmol) in 35 mL of a H_2O/CH_3CN mixture (1:6) was added. The deep blue solution was kept at room temperature overnight. Dark blue crystals formed, which were filtered off and dried under vacuum. Yield: 65%. Anal. Calcd for $C_{18}H_{15}O_{11}N_7S_2Cu_2$: C, 31.04; H, 2.17; N, 14.08. Found: C, 31.43; H, 2.28; N, 14.44. Although two water molecules show up in the X-ray structure of **4**, the elemental analysis clearly shows one water molecule is lost on drying.

Physical Measurements. Infrared spectra were recorded as Nujol mulls using a Mattson Polaris FT-IR instrument. Electronic spectra were recorded as mulls using Cary 17 and Cary 5E spectrometers. Room-temperature magnetic moments were measured using a Cahn 7600 Faraday magnetic balance, and variable-temperature magnetic data (5–300 K) were obtained using an Oxford Instruments superconducting Faraday susceptometer with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed, and $Hg[Co(NCS)_4]$ was used as a calibration standard.

Electrochemical measurements were made with a BAS CV-27 voltammograph and a Hewlett-Packard X-Y recorder. The electrochemical cell consisted of a Pt wire auxiliary electrode, a SCE reference electrode, and a glassy-carbon disk working electrode. All measurements were carried out in DMF (0.1 M TEAP, tetraethylammonium perchlorate), under a nitrogen atmosphere with 1 mM complex concentrations.

Elemental analyses were carried out by Canadian Microanalytical Laboratories, Delta, Canada.

Crystallographic Data Collection and Refinement of the Structures. (a) $[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$ (1). Crystals of **1** are green. The diffraction intensities of an approximately 0.40 × 0.20 × 0.15 mm parallelepiped crystal were collected with graphite-monochromatized Mo Kα radiation with a Rigaku AFC6S diffractometer using the ω–2θ scan mode to $2\theta_{max} = 50.0°$. A total of 2588 reflections were measured, of which 2514 were unique ($R_{int} = 0.050$) and 1393 were considered significant with $I_{net} > 3.0\sigma(I_{net})$. An empirical absorption correction was applied, using the program DIFABS,[33] which resulted in transmission factors ranging from 0.79 to 1.00. The data were corrected for Lorentz and polarization effects. The cell parameters were obtained from a least-squares refinement of the setting angles of 21 carefully centered reflections in the range $42.3° < 2\theta < 46.8°$.

Table I. Crystallographic Data for $[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$ (**1**), $[Cu_2(PTPH)(\mu_3\text{-}OH)(NO_3)_3(H_2O)]_2$ (**3**), and $[Cu_2(PTPH)(\mu_2\text{-}OH)(NO_3)_2(H_2O)_2](NO_3)$ (**4**)

	1	**3**	**4**
formula	$CuC_{10}H_{10}N_2SOCl_2$	$Cu_2C_{18}H_{15}N_7S_2O_{11}$	$Cu_2C_{18}H_{17}N_7S_2O_{12}$
fw	340.71	696.57	714.58
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	20.710(4)	12.075(2)	10.687(3)
b (Å)	11.694(3)	12.344(1)	13.472(3)
c (Å)	15.509(4)	8.728(2)	9.638(2)
α (deg)		97.78(1)	103.03(2)
β (deg)	133.85(1)	96.70(1)	90.75(2)
γ (deg)		110.390(9)	110.44(2)
V (Å^3)	2709(2)	1189.4(3)	1260.5(5)
ρ_{calcd} (g cm^{-3})	1.671	1.945	1.883
Z	8	2	2
μ (cm^{-1})	21.47	20.35	19.25
radiation, λ (Å)	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69
T (°C)	25	25	25
R^a	0.040	0.035	0.046
$R_w{}^b$	0.033	0.030	0.038

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

Table II. Final Atomic Positional Parameters and B_{eq} Values for $[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$ (**1**)

atom	x	y	z	$B_{eq}{}^a$ Å^2
Cu(1)	0.39946(5)	0.37138(7)	0.19203(7)	2.76(3)
Cl(1)	0.3136(1)	0.5269(1)	0.1270(2)	4.64(8)
Cl(2)	0.4398(1)	0.4163(2)	0.0926(2)	4.50(8)
S(1)	0.3018(1)	0.1254(2)	0.1327(1)	3.24(7)
O(1)	0.5957(8)	0.124(2)	0.559(1)	22(1)
N(1)	0.3597(3)	0.3128(4)	0.2715(5)	2.8(2)
N(2)	0.4565(3)	0.2120(4)	0.2236(4)	2.3(2)
C(1)	0.3712(4)	0.3774(6)	0.3534(6)	3.6(3)
C(2)	0.3422(5)	0.3419(6)	0.4073(6)	4.4(3)
C(3)	0.2982(5)	0.2400(7)	0.3729(7)	5.2(4)
C(4)	0.2877(5)	0.1714(5)	0.2918(7)	4.3(3)
C(5)	0.3186(4)	0.2121(5)	0.2416(6)	3.0(3)
C(6)	0.4146(4)	0.1146(5)	0.1987(5)	2.4(2)
C(7)	0.4546(4)	0.0058(5)	0.2221(5)	2.4(2)
C(8)	0.4106(4)	−0.0996(5)	0.1930(6)	3.8(3)
C(9)	0.4555(4)	−0.2000(5)	0.2216(7)	4.4(3)
C(10)	0.529(1)	0.064(3)	0.517(2)	38(3)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

The structure was solved by direct methods,[34,35] and the non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1393 reflections and 154 variable parameters and converged with $R = 0.040$ and $R_w = 0.033$, with weights based on counting statistics. The maximum and minimum peaks on the final difference map corresponded to 0.45 and −0.41 e/Å^3 respectively. Neutral-atom scattering factors[36] and anomalous-dispersion terms[37,38] were taken from the usual sources. All calculations were performed with the TEXSAN[39] crystallographic software package using a VAX 3100 work station. A summary of crystal and other data is given in Table I, and atomic coordinates are given in Table II. Hydrogen atom atomic coordinates (Table SI) and thermal parameters (Table SII) are included as supplementary material. The methanol oxygen O(1) and carbon C(10) were located, but the solvent molecule did not refine sensibly. However, the good overall refinement leaves no doubt as to the identity of the complex itself.

(b) $[Cu_2(PTPH)(\mu_3\text{-}OH)(NO_3)_3(H_2O)]_2$ (3) and $[Cu_2(PTPH)(\mu_2\text{-}OH)(NO_3)_2(H_2O)_2](NO_3)$ (4). Crystals of **3** are light blue. The diffraction intensities of an approximately 0.38 × 0.20 × 0.18 mm irregular crystal were collected, and the structure was solved in the same manner

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(33) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(34) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

(35) Beurskens, P. T. DIRDIF. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 655 Ed Nijmegen, The Netherlands, 1984.

(36) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A.

(37) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1974**, *17*, 781.

(38) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.3.1.

(39) *Texsan-Texray Structure Analysis Package*, Molecular Structure Corp.: Woodlands, TX, 1985.

Table III. Final Atomic Positional Parameters and B_{eq} Values for $[Cu_2(PTPH)(OH)(NO_3)_3(H_2O)]_2$ (**3**)

atom	x	y	z	$B_{eq}{}^a$ (Å^2)
Cu(1)	0.07238(5)	–0.05447(5)	0.11842(7)	1.86(2)
Cu(2)	0.22896(5)	0.22315(5)	0.20075(7)	2.09(2)
S(1)	0.1517(1)	–0.2086(1)	–0.1656(2)	2.36(5)
S(2)	0.4983(1)	0.3108(1)	0.0905(2)	2.86(5)
O(1)	0.0706(3)	0.1025(3)	0.1255(4)	1.8(1)
O(2)	–0.0726(3)	–0.1010(3)	0.2153(4)	2.7(1)
O(3)	0.1681(3)	0.3439(3)	0.2860(4)	2.8(1)
O(4)	0.0750(4)	0.4079(4)	0.4503(5)	5.5(2)
O(5)	0.0870(4)	0.2374(4)	0.4512(5)	4.2(2)
O(6)	0.2916(4)	0.1011(4)	0.6016(5)	6.1(2)
O(7)	0.1187(5)	–0.0214(5)	0.5248(6)	11.0(3)
O(8)	0.2242(3)	0.0302(3)	0.3540(4)	3.8(2)
O(9)	0.3291(4)	0.4817(3)	0.0658(5)	4.6(2)
O(10)	0.2269(3)	0.2988(3)	–0.0303(4)	3.8(2)
O(11)	0.2710(5)	0.4256(4)	–0.1795(6)	7.8(3)
N(1)	0.0887(3)	–0.2104(3)	0.1229(5)	2.1(2)
N(2)	0.2254(3)	0.0033(3)	0.0168(4)	1.6(1)
N(3)	0.3003(3)	0.1191(3)	0.0728(4)	1.8(1)
N(4)	0.3870(3)	0.3042(3)	0.3436(5)	2.1(2)
N(5)	0.1088(4)	0.3292(4)	0.3998(5)	2.9(2)
N(6)	0.2129(5)	0.0353(4)	0.4938(6)	3.7(2)
N(7)	0.2755(4)	0.4019(4)	–0.0522(6)	3.2(2)
C(1)	0.0676(5)	–0.2589(5)	0.2499(7)	3.0(2)
C(2)	0.0830(5)	–0.3627(5)	0.2667(7)	3.4(2)
C(3)	0.1233(5)	–0.4181(5)	0.1510(8)	3.4(2)
C(4)	0.1468(5)	–0.3688(4)	0.0193(7)	2.7(2)
C(5)	0.1286(4)	–0.2654(4)	0.0105(6)	2.0(2)
C(6)	0.2545(4)	–0.0626(4)	–0.0906(5)	1.7(2)
C(7)	0.3615(4)	–0.0206(4)	–0.1556(5)	1.7(2)
C(8)	0.3943(5)	–0.0910(4)	–0.2683(6)	2.4(2)
C(9)	0.5002(5)	–0.0435(5)	–0.3216(6)	3.0(2)
C(10)	0.5745(5)	0.0730(5)	–0.2665(7)	3.2(2)
C(11)	0.5452(4)	0.1437(5)	–0.1560(6)	2.5(2)
C(12)	0.4382(4)	0.0972(4)	–0.0970(5)	1.9(2)
C(13)	0.4017(4)	0.1631(4)	0.0216(6)	1.8(2)
C(14)	0.4931(4)	0.3319(4)	0.2941(6)	2.2(2)
C(15)	0.6018(5)	0.3840(4)	0.3963(7)	2.9(2)
C(16)	0.6013(5)	0.4065(5)	0.5563(7)	3.4(2)
C(17)	0.4937(5)	0.3765(5)	0.6086(6)	3.1(2)
C(18)	0.3884(5)	0.3255(4)	0.4990(6)	2.8(2)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

as described for **1**. Crystal and other data are listed in Table I, and atomic coordinates are listed in Table III. Hydrogen atom coordinates (Table SIII) and thermal parameters (Table SIV) are included as supplementary material.

Crystals of **4** are deep blue. The diffraction intensities of an approximately 0.30 × 0.25 × 0.15 mm parallelepiped crystal were collected, and the structure was solved in the same manner as described for **1**. Crystal and other data are listed in Table I, and atomic coordinates are listed in Table IV. Hydrogen atom coordinates (Table SV) and thermal parameters (Table SVI) are included as supplementary material.

Results and Discussion

X-ray Crystal Structures. (a) $[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$ (1). A perspective view of **1** is shown in Figure 1, and selected bond distances and angles relevant to the copper coordination spheres are given in Table V. The two square-pyramidal copper centers are bridged by three groups, the diazine N_2 and two chlorine atoms. The ligand adopts a pronounced *anti* twist, creating an angle of 56.5° between the copper square planes and angles of 53.1° between the copper planes and the phthalazine plane. The copper center is displaced slightly from the N_2Cl_2 least-squares plane by 0.154(5) Å, and the pyridine mean planes are twisted by 52.7° with respect to the phthalazine mean plane. The in-plane copper–nitrogen and copper–chlorine distances are relatively short and compare closely with those observed for the analogous pyridazine complex $[Cu_2(PTP)Cl_4]$[30] (PTP = 3,6-bis(2-pyridylthio)pyridazine), which has the same tribridged structure. The chlorine atoms each bridge the two copper centers by a short (2.266(2) Å) equatorial bond and a long (2.666(2) Å) axial bond, in an asymmetric arrangement.

Table IV. Final Atomic Positional Parameters and B_{eq} Values for $[Cu_2(PTPH)(OH)(NO_3)_2(H_2O)_2](NO_3)$ (**4**)

atom	x	y	z	$B_{eq}{}^a$ (Å^2)
Cu(1)	0.1948(1)	0.10372(8)	–0.1777(1)	2.60(4)
Cu(2)	0.0691(1)	0.25514(8)	–0.2758(1)	2.64(4)
S(1)	0.4476(2)	0.2239(2)	0.0939(3)	3.4(1)
S(2)	0.1582(2)	0.5117(2)	–0.0848(2)	3.2(1)
O(1)	0.0321(5)	0.1308(4)	–0.2009(6)	2.8(2)
O(2)	0.1045(6)	–0.0490(4)	–0.2875(6)	3.8(2)
O(3)	0.1463(6)	0.0438(5)	0.0341(6)	4.1(3)
O(4)	–0.0958(7)	0.1853(5)	–0.4137(7)	4.4(3)
O(5)	–0.1517(7)	0.2901(6)	–0.244(1)	6.3(4)
O(6)	–0.2942(7)	0.1950(6)	–0.4290(9)	7.1(4)
O(7)	–0.1249(7)	0.1985(6)	0.1522(9)	6.3(4)
O(8)	–0.0013(7)	0.3482(6)	0.1070(8)	5.7(3)
O(9)	0.0898(6)	0.2433(5)	0.1676(7)	4.7(3)
O(10)	0.255(1)	0.1837(7)	–0.409(1)	9.6(5)
O(11)	0.305(2)	0.191(2)	–0.609(2)	9.5(6)
O(12)	0.187(2)	0.044(2)	–0.569(2)	8.2(5)
O(13)	0.099(2)	0.129(1)	–0.509(2)	9.3(5)
O(14)	0.209(2)	0.083(2)	–0.645(2)	10.1(6)
N(1)	0.3748(7)	0.0880(5)	–0.1724(7)	2.6(3)
N(2)	0.2810(6)	0.2654(5)	–0.0736(6)	2.0(2)
N(3)	0.2190(6)	0.3315(5)	–0.1138(6)	2.1(2)
N(4)	0.1272(6)	0.3865(5)	–0.3552(7)	2.3(3)
N(5)	–0.1849(9)	0.2231(7)	–0.362(1)	4.7(4)
N(6)	–0.0109(9)	0.2633(7)	0.1411(8)	3.6(3)
N(7)	0.230(1)	0.1372(9)	–0.528(1)	6.6(5)
C(1)	0.401(1)	0.0198(8)	–0.285(1)	4.0(4)
C(2)	0.517(1)	–0.0007(9)	–0.291(1)	5.0(5)
C(3)	0.616(1)	0.052(1)	–0.177(1)	5.2(5)
C(4)	0.5934(8)	0.1245(8)	–0.064(1)	3.8(4)
C(5)	0.4711(9)	0.1395(7)	–0.065(1)	2.8(3)
C(6)	0.3685(7)	0.3055(6)	0.0409(9)	2.2(3)
C(7)	0.3985(7)	0.4120(6)	0.1306(9)	2.2(3)
C(8)	0.4878(8)	0.4548(7)	0.255(1)	3.1(4)
C(9)	0.5162(8)	0.5596(8)	0.333(1)	3.5(4)
C(10)	0.4567(8)	0.6259(7)	0.290(1)	3.3(4)
C(11)	0.3676(8)	0.5867(7)	0.170(1)	2.6(3)
C(12)	0.3369(8)	0.4792(6)	0.0874(9)	2.3(3)
C(13)	0.2439(7)	0.4318(6)	–0.0385(8)	2.1(3)
C(14)	0.1622(7)	0.4894(6)	–0.2732(9)	2.3(3)
C(15)	0.1954(8)	0.5790(7)	–0.329(1)	3.0(4)
C(16)	0.1969(9)	0.5636(8)	–0.475(1)	3.8(4)
C(17)	0.1642(9)	0.4603(8)	–0.559(1)	3.7(4)
C(18)	0.1309(8)	0.3751(7)	–0.496(1)	3.3(4)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

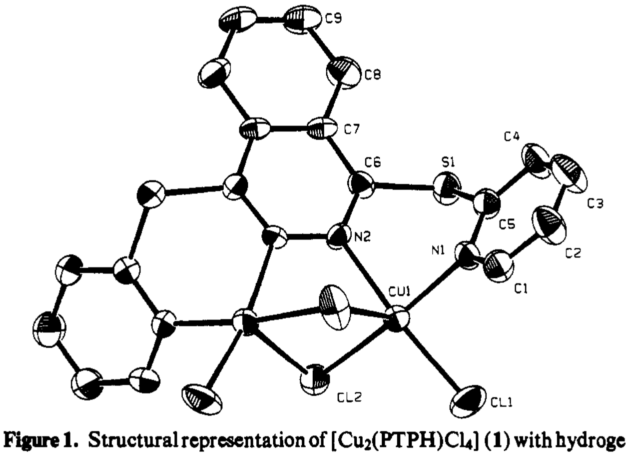

Figure 1. Structural representation of $[Cu_2(PTPH)Cl_4]$ (**1**) with hydrogen atoms omitted (40% probability thermal ellipsoids).

(b) $[Cu_2(PTPH)(OH)(NO_3)_3(H_2O)]_2$ (3). A perspective view of **3** is shown in Figure 2, and selected bond distances and angles relevant to the copper coordination spheres are given in Table VI. Each copper center is bonded by short, in-plane, contacts to two nitrogen and two oxygen atoms, with the hydroxide oxygen O(1) and the diazine nitrogen pair N(2)–N(3) acting as bridges between the two metal atoms. A water molecule (O(2)) is bound terminally to Cu(1), while equatorial oxygen O(3), bound to Cu(2), arises from a monodentate nitrate. Somewhat longer, but nevertheless

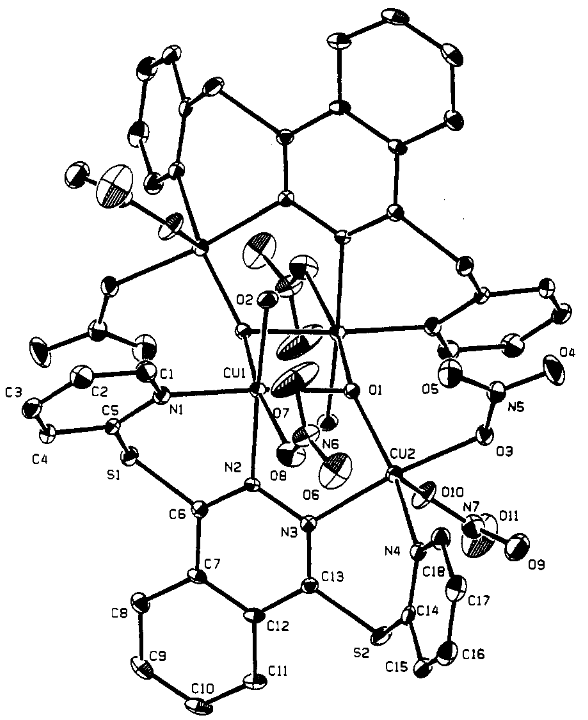

Figure 2. Structural representation of $[Cu_2(PTPH)(OH)(NO_3)_3(H_2O)]_2$ (3) with hydrogen atoms omitted (40% probability thermal ellipsoids).

Table V. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$ (1)

Cu(1)–N(1)	2.017(5)	Cu(1)–Cl(2)	2.266(2)
Cu(1)–N(2)	2.076(4)	Cu(1)–Cl(2)′	2.666(2)
Cu(1)–Cl(1)	2.236(2)	Cu(1)–Cu(1)′	3.1194(2)
Cl(1)–Cu(1)–Cl(1)	93.27(7)	Cl(2)–Cu(1)–N(2)	87.2(1)
Cl(1)–Cu(1)–N(1)	91.1(1)	N(1)–Cu(1)–N(2)	87.6(2)
Cl(1)–Cu(1)–N(2)	169.0(1)	Cu(1)–Cl(2)–Cu(1)′	80.35(9)
Cl(2)–Cu(1)–N(1)	173.2(2)		

Table VI. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(PTPH)(OH)(NO_3)_3(H_2O)]_2$

Cu(1)–O(1)	1.938(3)	Cu(2)–O(3)	1.977(3)
Cu(1)–O(2)	1.971(3)	Cu(2)–N(3)	2.060(4)
Cu(1)–N(1)	2.007(4)	Cu(2)–N(4)	1.993(4)
Cu(1)–N(2)	2.084(4)	Cu(2)–O(10)	2.336(4)
Cu(1)–O(8)	2.426(4)	Cu(1)–Cu(2)	3.215(1)
Cu(1)–O(1)	2.440(3)	Cu(1)–Cu(1)′	3.269(1)
Cu(2)–O(1)	1.940(3)		
O(1)–Cu(1)–O(2)	90.7(1)	O(1)–Cu(2)–N(4)	156.1(2)
O(1)–Cu(1)–N(1)	174.9(1)	O(3)–Cu(2)–N(3)	167.1(1)
O(1)–Cu(1)–N(2)	86.4(1)	O(3)–Cu(2)–N(4)	91.9(1)
O(2)–Cu(1)–N(1)	91.9(1)	N(3)–Cu(2)–N(4)	89.8(2)
O(2)–Cu(1)–N(2)	177.1(1)	O(10)–Cu(2)–N(4)	111.0(1)
O(8)–Cu(1)–O(1)	86.0(1)	O(10)–Cu(2)–O(3)	86.2(1)
O(8)–Cu(1)–O(2)	99.5(1)	O(10)–Cu(2)–O(1)	92.4(1)
O(8)–Cu(1)–N(1)	89.3(1)	O(10)–Cu(2)–N(3)	81.3(1)
O(8)–Cu(1)–N(2)	80.3(1)	Cu(1)–O(1)–Cu(2)	112.0(1)
O(1)–Cu(2)–O(3)	94.5(1)	Cu(1)–O(1)–Cu(1)′	95.9(1)
O(1)–Cu(2)–N(3)	89.1(1)	Cu(1)′–O(1)–Cu(2)	132.6(1)

significant, contacts (Cu(1)–O(8) = 2.426(4) Å; Cu(2)–O(10) = 2.336(4) Å; Cu(1)′–O(1) = 2.440(3) Å) indicate additional ligands on Cu(1) and Cu(2). The second symmetry-related Cu(1)′–O(1) contact clearly indicates that the molecule is a dimer, with a most unusual fusion of two dinuclear centers. Cu(2) is therefore square-pyramidal, while Cu(1) is a tetragonally distorted octahedron. The hydroxide (O(1)) bridges Cu(1) and Cu(2) in the traditional manner but also acts as a bridge between two symmetry-related Cu(1) centers, thus acting as a μ_3-hydroxide. The solid angle at O(1) (340.5°) indicates substantial pyramidal distortion at the μ_3-hydroxide bridge. The Cu(1)–Cu(1)′ distance is therefore quite short (3.269(1) Å) and comparable with the Cu(1)–Cu(2) separation (3.215(1) Å). The four copper centers are therefore linked through both the diazine and hydroxide bridges, involving the fusion of the two five-membered Cu_2N_2O rings to the central Cu_2O_2 ring. O(1) links Cu(1) and Cu(2) equatorially, whereas the dimer linkage involves a combination of axial and equatorial bonds to Cu(1).

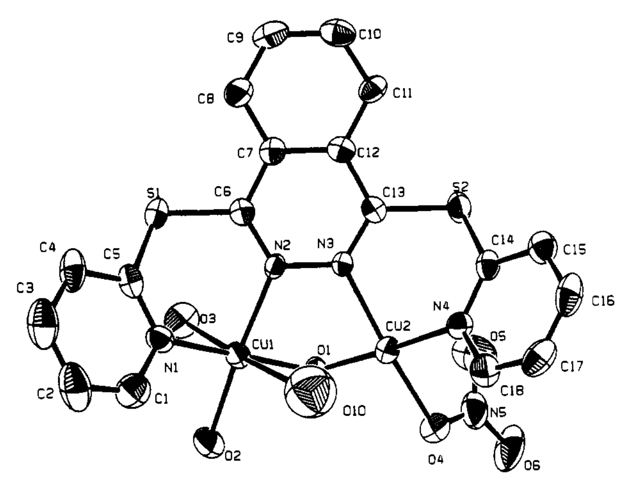

Figure 3. Structural representation of $[Cu_2(PTPH)(OH)(NO_3)_2(H_2O)_2](NO_3)$ (4) with hydrogen atoms omitted (40% probability thermal ellipsoids).

The conformation of the ligand contrasts sharply with that in **1**, with a *syn* arrangement of the pyridine rings, leading to the mutual equatorial bridging arrangement of the hydroxide. The pyridine rings (defined by N(1) and N(4)) have dihedral angles of 56.4 and 50.5°, respectively, with respect to the mean phthalazine plane. The $Cu(1)N_2O_2$ square plane has a substantial tetrahedral distortion, with a mean deviation from the plane of 0.253(4) Å. The CuN_2O_2 least-squares planes are inclined by 97.1°. The large copper–copper distance (3.215(1) Å) and Cu(1)–O(H)–Cu(2) angle (112.0(1)°) are normally typical of phthalazine complexes involving axial, bidentate bridging anions, e.g. IO_3^-, NO_3^-, SO_4^{2-}, which have the effect of forcing the metal centers apart.[21] The absence of such a group in this case is unusual but parallels the situation found for the tetranuclear copper complexes $[Cu_4(TNL4Me)(\mu_2\text{-}OH)_2(H_2O)_8](CF_3SO_3)_6$ and $[Cu_4(TNL)(\mu_2\text{-}OH)_2(H_2O)_6(EtOH)_2](CF_3SO_3)_6$ (ligand = 1,4,6,9-tetrakis((R–2-pyridyl)amino)benzodipyridazine (TNL, R = H; TNL4Me, R = 4-Me)), which have large Cu–O(H)–Cu angles (116.3(3) and 116.0(5)°, respectively) and only the diazine and hydroxide groups bridging the copper pairs in an equatorial fashion.[40,41] The *syn* folding of the ligand leads to a corresponding folding of the dinuclear center, such that the hydroxide bridge O(1)H projects below the dicopper center significantly (0.78 Å from the Cu(1)Cu(2)N(2)N(3)O(2)O(3) mean plane).

(c) $[Cu_2(PTPH)(OH)(NO_3)_2(H_2O)_2](NO_3)$ (4). A perspective view of **4** is shown in Figure 3, and selected bond distances and angles relevant to the copper coordination spheres are given in Table VII. Superficially **4** and **3** appear to be very similar, but their marked color differences, and differences in their electronic spectra, indicate that there are perhaps significant structural differences. **4** involves the same *syn* ligand conformation, with two N_2O_2 equatorial donor sets, with relatively short contacts, arranged around each copper center, with the two metals bridged by both diazine and hydroxide groups. The in-plane ligand distances compare very closely with those observed for **3**. The Cu–Cu separation (3.101(2) Å) and Cu–O(H)–Cu angle (109.0(3)°) are slightly smaller than those found in **3**. However there

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(40) Tandon, S. S.; Mandal, S. K.; Thompson, L. K.; Hynes, R. C. *J. Chem. Soc., Chem. Commun.* **1991**, 1572.

(41) Tandon, S. S.; Mandal, S. K.; Thompson, L. K.; Hynes, R. C. *Inorg. Chem.* **1992**, *31*, 2215.

Table VII. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in [Cu$_2$(PTPH)(OH)(NO$_3$)$_2$(H$_2$O)$_2$](NO$_3$) (**4**)

Cu(1)–O(1)	1.918(5)	Cu(2)–O(1)	1.891(5)
Cu(1)–O(2)	1.973(5)	Cu(2)–O(4)	1.993(6)
Cu(1)–N(1)	2.008(7)	Cu(2)–N(3)	2.031(6)
Cu(1)–N(2)	2.046(6)	Cu(2)–N(4)	1.990(6)
Cu(1)–O(3)	2.360(6)	Cu(2)–O(13)	2.59(2)
Cu(1)–O(10)	2.676(6)	Cu(1)–Cu(2)	3.101(2)
O(1)–Cu(1)–O(2)	90.1(2)	O(10)–Cu(1)–N(2)	82.2(3)
O(1)–Cu(1)–N(1)	172.2(3)	O(1)–Cu(2)–O(4)	92.8(2)
O(1)–Cu(1)–N(2)	86.7(2)	O(1)–Cu(2)–N(3)	86.0(2)
O(2)–Cu(1)–N(1)	92.4(3)	O(1)–Cu(2)–N(4)	174.1(2)
O(2)–Cu(1)–N(2)	175.9(3)	O(4)–Cu(2)–N(3)	171.6(3)
N(1)–Cu(1)–N(2)	90.5(3)	O(4)–Cu(2)–N(4)	91.3(3)
O(3)–Cu(1)–O(1)	96.1(2)	N(3)–Cu(2)–N(4)	90.5(3)
O(3)–Cu(1)–O(2)	88.3(2)	O(13)–Cu(2)–O(1)	84.3(4)
O(3)–Cu(1)–N(1)	91.6(2)	O(13)–Cu(2)–O(4)	66.5(5)
O(3)–Cu(1)–N(2)	94.7(2)	O(13)–Cu(2)–N(3)	121.4(5)
O(10)–Cu(1)–O(1)	83.0(3)	O(13)–Cu(2)–N(4)	93.4(5)
O(10)–Cu(1)–O(2)	94.7(3)	Cu(1)–O(1)–Cu(2)	109.0(3)
O(10)–Cu(1)–N(1)	89.3(3)		

is no indication that a dimeric structure exists in this case, and a simpler dinuclear entity exists, typical of this sort of complex. Copper atom Cu(1) has a water molecule bound axially (Cu(1)–O(3) = 2.360(6) Å) and another water molecule bound equatorially (Cu(1)–O(2) = 1.973(5) Å), but the long contact to O(10) (Cu(1)–O(10) = 2.676(9) Å) indicates a weak axial interaction with the disordered N(7) nitrate. O(10) has been refined at unit occupancy, but the other nitrate oxygens O(11), O(12), O(13), and O(14) have been refined at half-occupancy. The Cu(2)–O(13) separation of 2.59(2) Å may be considered to be a bonding interaction in half the molecules (defined by the disorder model), and so crystallographically the N(7) nitrate appears to be "partially" bidentate. Cu(1) is therefore best represented as a tetragonally distorted octahedral copper center. Copper atom Cu(2) is bound by close in-plane contacts to two ligand nitrogens, hydroxide O(1), and a monodenate nitrate (O(4)) and so has a pseudo-square-planar structure.

Spectroscopy and Magnetism. Infrared spectra of **1** and **2** are very similar in the range 4000–500 cm^{-1}, indicating the likelihood of a similar dinuclear structural arrangement in **2**. In the far-infrared two prominent bands at 300 and 275 cm^{-1} for **1** (associated with terminal and bridging copper–chlorine bonds, respectively) are shifted to 285 and 245 cm^{-1} in **2**, confirming the mixed terminal and bridging arrangement of bromine ligands.

Electronic spectra (mull transmittance) for **1** and **2** have visible absorptions at similar energies (14 000 and 14 300 cm^{-1}, respectively), which is somewhat surprising, considering the likely structural similarities and the different ligands. However charge-transfer bands at 25 000 cm^{-1} (**1**) and 20 000 cm^{-1} (**2**) clearly differentiate the two compounds and are associated with halogen to metal charge transfer. **3** and **4** have very similar visible absorptions (16 370 and 16 560 cm^{-1}, respectively), which is not surprising considering the similarities in donor sets.

Room-temperature magnetic moments for all the complexes are subnormal (Table VIII), falling in the range 1.34–1.62 μ_B, indicating spin coupling between the copper(II) centers and the presence of net antiferromagnetism. Variable-temperature (5–300 K) magnetic data were obtained for **1**–**4**. A plot of the experimental susceptibility data for **1** is given in Figure S1 (see supplementary material). The data for **1**–**4** were fitted to the Bleaney–Bowers expression (eq 1),[42] using the isotropic (Heisenberg) exchange Hamiltonian ($\mathcal{H} = -2JS_1S_2$) for two interacting S=$^1/_2$ centers (χ_m is expressed per mole of copper atoms, $N\alpha$ is the temperature-independent paramagnetism (60 × 10^{-6} cgsu per copper), ρ is the fraction of monomeric impurity, and Θ is a corrective term for interdimer interactions[43,44]) and a nonlinear regression procedure. The best fit data are presented in Table VIII and graphically in Figure S1 for **1**.

$$\chi_m = \frac{N\beta^2g^2}{3k(T-\Theta)}[1 + {}^1/_3 \exp(-2J/kT)]^{-1}(1-\rho) + \frac{[N\beta^2g^2]\rho}{4kT} + N\alpha \quad (1)$$

As in the previous cases, where structurally similar copper halide complexes of pyridazine ligands are compared,[22] exchange is stronger for the bromo complex of PTPH. The only viable superexchange route for antiferromagnetic coupling in **1** and **2** occurs through the diazine bridge, and a comparison of **1** and **2** with isostructural complexes of the ligand PTP (3,6-bis(2-pyridylthio)pyridazine) reveals that exchange for the pyridazine complexes is larger than that associated with corresponding phthalazine complexes, indicating again the capacitive nature of the fused benzene ring in the phthalazine entity.[21,22,27] These results complement an earlier study on linear-chain complexes Cu$_2$LX$_2$ (L = pyridazine, phthalazine; X = Cl, Br), which were treated using both Heisenberg and Ising models. Net antiferromagnetic behavior was observed in all cases, and significantly larger exchange integrals were evident for the pyridazine-bridged complexes.[45] Unfortunately no structures were reported.

Compound **4** resembles some copper nitrate complexes of the PAPR [1,4-bis(2-pyridyl(R)amino)phthalazine] ligands, in which comparable dinuclear center dimensions were observed, with Cu–(OH)–Cu angles in the range 112.6–115.5°, and yet larger exchange integrals were found ($-2J$ = 497–597 cm^{-1}).[21] On the basis of the linear relationship between $-2J$ and the Cu–(OH)–Cu angle in the PAPR series of complexes as a whole,[21] the angle of 109.0° found in **4** would correspond to a $-2J$ value of 370 cm^{-1}, which is somewhat larger than that found in **4**, but because of the ligand differences, and in particular the longer linkages between the exocyclic sulfur atoms and the phthalazine and pyridine rings, the agreement is satisfying.

The fitting of the variable-temperature data for **3** to the Bleaney–Bowers equation gave a very good data analysis (Table VIII) with a value of $-2J$ comparable with that found for **4**. The Cu–O(H)–Cu bridge angle within each dinuclear half of the dimeric structure (112.0°) is somewhat larger than that for **4** and does not fit the exchange/bridge angle relationship established for the (pyridylamino)phthalazine complexes[21] ($-2J_{\mathrm{calcd}}$ = 440 cm^{-1}) very well. One is now drawn to the nature of the dimerization and the possible magnetic connections. Although the Cu(1)–O(1) dimer distance (2.440(3) Å), within the Cu$_2$O$_2$ ring, is a significant bonding contact, it links the dinuclear halves via an axial orbital interaction, which will not contribute in an antiferromagnetic sense. If any significant interdinuclear interaction existed, it would show up in the θ corrective term included in the Bleaney–Bowers equation. In this case, even though the Θ value (0.2 K) indicates possible ferromagnetic interdinuclear coupling, consistent with the orbital argument, the very small value indicates an insignificant interaction. Also the result indicates that treating the data with a trinuclear or even tetranuclear model would not improve the data fit. With a simple μ_2-hydroxide bridge it is difficult to estimate the degree of trigonal distortion at the oxygen atom itself, because of the difficulty of accurately locating the bonded hydrogen atom. In this case the solid angle at O(1) is 340.5°, indicating substantial pyramidal distortion. A strictly planar (sp^2) geometry at the bridging oxygen, coupled with coplanarity of the copper equatorial planes, can lead to efficient magnetic overlap via the bridge atom and strong antiferromagnetic exchange, if the angle Cu–O(H)–Cu is sufficiently large.[21] A pyramidal distortion at the oxygen bridge

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(42) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451.

(43) McGregor, K. T.; Barnes, J. A.; Hatfield, W. E. *J. Am. Chem. Soc.* **1973**, *95*, 7993.

(44) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490.

(45) Emori, S.; Inoue, I.; Kubo, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2259.

Table VIII. Structural and Magnetic Data[a]

compd	Cu–Cu (Å)	Cu–O–Cu (deg)	μ_{eff} (RT)	$-2J$ (cm^{-1})	g	ρ	Θ (K)	R
$[Cu_2(PTPH)Cl_4]\cdot 2CH_3OH$ (**1**)	3.194(2)		1.62	124(2)	2.10(3)	0.003	−1.0	0.59
$[Cu_2(PTPH)Br_4]\cdot 1.5H_2O$			1.52	174(5)	2.03(6)	0.005	1.0	0.76
$[Cu_2(PTPH)(OH)(NO_3)_3(H_2O)]_2$ (**3**)	3.215(1)	112.0(1)	1.28	313(2)	2.043(7)	0.007	0.2	0.34
$[Cu_2(PTPH)(OH)(NO_3)_2(H_2O)_2](NO_3)$ (**4**)	3.101(2)	109.0(3)	1.34	308(5)	2.03(4)	0.006	−0.2	0.79

[a] $R = [\sum(\chi_{obsd} - \chi_{calcd})^2/\sum(\chi_{obsd})^2]^{1/2} \times 10^2$; $N\alpha = 60 \times 10^{-6}$ cgsu in all cases.

(approaching sp^3) leads to a situation where less efficient magnetic orbital overlap with the oxygen bridge occurs, thus reducing antiferromagnetic coupling, and in some cases can lead to ferromagnetic coupling.[46–49] Such a situation is often accompanied by a bending of the copper equatorial planes as well, which leads to reduced antiferromagnetic coupling, particularly in "roof-shaped" dihydroxo-bridged dicopper complexes.[50] A further argument can be advanced for reduced antiferromagnetic exchange in **3** by considering the additional bonds between O(1) and the neighboring Cu(1) atoms, which would act as Lewis acids toward O(1) and effectively polarize the electron density on the oxygen bridge to a larger extent than would be the case for **4**.

Cyclic voltammetry for **1** and **2** in dried DMF shows a single nonreversible wave ($\Delta E_p \approx 160$ mV at 200 mV s^{-1}) in the range 0–0.5 V ($E_{1/2} = 0.430$ V (**1**), 0.425 V (**2**) vs SCE), associated with sequential two-electron reduction of the dinuclear complex to a dinuclear copper(I) species. Controlled-potential electrolysis in DMF at a potential of 0.1 V indicated the passage of approximately 2 electron equiv of charge. The nonreversible behavior indicates the likelihood of a molecular rearrangement on reduction to a dinuclear copper(I) species, and this is strongly supported by the independent synthesis of the complex $[Cu(PTPH)]_2(ClO_4)_2$ (from $Cu^I(ClO_4)$ and PTPH), which contains a dinuclear cation in which two tetrahedral metals are bonded between two tetradentate ligands.[51] A similar situation was observed for complexes of the corresponding pyridazine ligand PTP.[31,51] Compounds **3** and **4** did not dissolve appreciably in suitable solvents and were not examined electrochemically.

Conclusions

PTPH acts as a typical tetradentate N_4 diazine ligand producing dinuclear complexes with copper(II) salts, in which the two copper centers are antiferromagnetically coupled. However, in a most unusual reaction involving copper(II) nitrate, two very different complexes, one dinuclear and the other tetranuclear, are produced by employing slight and subtle differences in reaction conditions. The tetranuclear, dimerized dinuclear derivative involves μ_3-hydroxide groups with substantial pyramidal distortion, which is seen as a contributing factor to lower than expected antiferromagnetic exchange. The magnetic properties of **1** and **2**, when compared internally, and with those of analogous and isostructural pyridazine complexes, again indicate the dominant polarizing effect of electronegative ligands like chlorine and the capacitive nature of fused benzene rings in diazine-bridged systems.

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Supplementary Material Available: Tables listing detailed crystallographic data, hydrogen atom positional parameters, anisotropic thermal parameters, bond lengths and angles, and least-squares planes and a plot of χ_m versus T for **1** (29 pages). Ordering information is given on any current masthead page.

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(46) Iliopoulos, P.; Murray, K. S.; Robson, R.; Wilson, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1585.

(47) Murray, K. S. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: New York, 1986; Vol. 2, p 161.

(48) Mazurek, W.; Kennedy, B. J.; Murray, K. S.; O'Connor, M. J.; Snow, M. R.; Rodgers, J. R.; Wedd, A. G.; Zwack, P. R. *Inorg. Chem.* **1985**, *24*, 3258.

(49) Mazurek, W.; Berry, K. J.; Murray, K. S.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1982**, *21*, 3071.

(50) Charlot, M. F.; Kahn, O.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1410.

(51) Chen, L.; Thompson, L. K. Unpublished results.