tography (UV/vis (nm): 410, 567) was dissolved in $CHCl_3$ and treated with 30 drops of water and 30 drops of concentrated HCl. Anal. Calcd for $FeC_{60}H_{28}O_4F_{28}N_8Cl$: C, 46.55; H, 1.82; N, 7.24; F, 34.36; Cl, 2.29. Found: C, 46.42; H, 2.03; N, 7.40; F, 34.35; Cl, 2.51. ^{19}F NMR (ppm vs. external Freon-F11): −64.3 (3 F), −73.0 (2 F), −116.2 (2 F). UV/vis (nm): 415, 498, 570.

Fe(α^4FPP-3) and (α^4FPP-3)FeOFe(α^4FPP-3). In a drybox, $K(Et_3)H$ (320 μL, 1.0 M solution from Aldrich) was added dropwise to a solution of Fe(FPP-3)Cl (0.50 g, 0.32 mmol) in THF (200 mL) at −35 °C. It was warmed to room temperature and stirred for 45 min. The solution was rotovapped to dryness. Dry degassed toluene was added, the solution filtered through a Teflon membrane and the solvent removed in vacuo. The remaining solid was pumped on to remove Et_3B, dissolved in CH_2Cl_2, and crystallized with heptane. Yield: 0.27 g, 55%. ^{19}F NMR (in toluene-d_8, ppm vs. external Freon-F11): −88.6 (3 F, −129.8 (2 F), −134.7 (2 F). UV/vis (nm): 430, 533, 560. The ^{19}F NMR spectrum was also recorded for the bis(pyridine) adduct Fe(FPP-3)$(py)_2$. ^{19}F NMR (in toluene-d_8, ppm vs. external Freon-F11): −81.5 (t, 3 F), −121.3 (q, 2 F), −127.9 (s, 2 F).

To convert the product to the μ-oxo dimer, dry dioxygen was bubbled through a solution of Fe(FPP-3) in dry toluene for 15 min, and then the toluene was removed in vacuo. ^{19}F NMR (ppm vs external Freon-F11): −82.7 (3 F), −123.3 (2 F), −129.4 (2 F). UV/vis (nm): 404, 565.

Fe(α^4FPP-7)Br. The procedure described for Fe(FPP-3)Br was followed. Yield: 0.147 g, 13.9%. Anal. Calcd for $FeC_{76}H_{28}N_8O_4F_{60}Br$: C, 38.15; H, 1.18; N, 4.68; F, 47.64. Found: C, 40.36; H, 1.67; N, 4.65; F, 47.85. UV/vis (nm): 417, 504, 570, 639.

Fe(α^4HPP-7)Br. The procedure described for Fe(FPP-3)Br was followed. Yield: 0.340 g, 30.5%. Anal. Calcd for $FeC_{76}H_{88}N_8O_4Br$: C, 69.50; H, 6.75; N, 8.53. Found: C, 69.61; H, 6.94; N, 8.47. UV/vis (nm): 415, 509, 581.

Fe($T_{2\text{-Me}}$PP)Cl. Iron powder (0.50 gm) and glacial acetic acid (500 mL) were added to a round-bottom flask equipped with a reflux condenser and nitrogen inlet. The apparatus was attached to a Schlenk line and pump–flushed seven times, and the solution was refluxed for 24 h. $H_2T_{2\text{-Me}}PP$ (1.0 g, 1.49 mmol) and NaCl (0.50 g) were added to $CHCl_3$ (25 mL). This mixture was stirred for 15 min and added to the reaction, and the reaction solution was refluxed for 2 h. The volume was reduced to 50 mL and 50 mL of water added. This mixture was sonicated and filtered, and the solid was dried on a high-vacuum line. The crude material was purified by column chromatography on acid alumina, eluting with $CHCl_3$. A light pink band was discarded and was followed by a major dark band, which was collected and rotovapped down to ~100 mL. Heptane (100 mL) was added and the solvent volume slowly reduced on a rotoevaporator until a precipitate formed, and then the mixture was refrigerated overnight. Yield: 0.537 g, 44.8%. Anal. Calcd for $FeC_{48}H_{36}N_4Cl$: C, 75.85: H, 4.77; N, 7.37; Cl, 4.66. Found: C, 76.01, H, 5.25; N, 7.10; Cl, 4.88. UV/vis (nm): 376, 415, 507, 575.

Fe($T_{2,4,6\text{-MeO}}$PP)Cl (E26585-17). The procedure described for Fe($T_{2\text{-Me}}$PP)Cl was followed. Yield: 74.4%. UV/vis (nm): 418, 509, 586.

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Registry No. Fe($T_{4\text{-Me}}$PP)Cl, 19496-18-5; Fe($T_{3\text{-Me}}$PP)Cl, 52155-49-4; Fe($T_{2\text{-Me}}$PP)Cl, 52155-50-7; Fe($T_{3,4,5\text{-MeO}}$PP)Cl, 81245-21-8; Fe($T_{2,4,6\text{-MeO}}$PP)Cl, 53470-05-6; Fe($T_{2\text{-F}}$PP)Cl, 98858-68-5; Fe($T_{F\text{-}5}$PP)Cl, 36965-71-6; Fe(α-FPP-3)Cl, 98858-69-6; Fe(α-FPP-3)Br, 98858-70-9; Fe(α-FPP-7)Br, 98858-71-0; Fe(α-HPP-7)Br, 98858-72-1; FePc, 132-16-1; FeFPc, 23844-93-1; Fe(TPP)Cl, 16456-81-8; cyclohexane, 110-82-7; *n*-pentane, 109-66-0; *n*-octane, 111-65-9; methylcyclohexane, 108-87-2; *tert*-butylcyclohexane, 3178-22-1; ethylbenzene, 100-41-4.

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Binuclear Copper(II) Complexes of a Series of Tetradentate Pyrazolyldiazines. Crystal and Molecular Structures of [μ-3,6-Bis(3,5-dimethyl-1-pyrazolyl)pyridazine-N,μ-N^3,μ-$N^{3'}$,N](μ-hydroxo)dichlorodicopper(II) Aquotrichlorocuprate Hydrate, $Cu_3C_{14}H_{21}Cl_5N_6O_3$, and [$\mu$-3,6-Bis(3,5-dimethyl-1-pyrazolyl)pyridazine-N,μ-N^6,μ-N^7,N](μ-hydroxo)tris(nitrato)diaquodicopper(II) Hydrate, $Cu_2C_{14}H_{23}N_9O_{13}$

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Binucleating pyrazolylpyridazine and phthalazine ligands form predominantly binuclear copper(II) complexes in which, in many cases, the metal centers are bridged by a hydroxide group in addition to the diazine bridge. Low magnetic moments for these species (μ_{eff}(room temperature) < 0.74 μ_B) indicate strong spin exchange between the copper(II) centers. One complex, $Cu_2(PPD)(OH)Br_3\cdot 1.5H_2O$ (PPD = 3,6-bis(1-pyrazolyl)pyridazine), was found to be diamagnetic at room temperature. The crystal and molecular structures of $[Cu_2(PPDMe)(OH)Cl_2][CuCl_3(H_2O)]\cdot H_2O$ (V) and $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII) (PPDMe = 3,6-bis(3,5-dimethyl-1-pyrazolyl)pyridazine) are reported. The trinuclear species (V) contains the unusual tetrahedrally distorted anion $[CuCl_3(H_2O)]^-$ and a binuclear hydroxo-bridged cation. V crystallized in the monoclinic system, space group *Am*, with a = 7.4942 (4) Å, b = 20.418 (1) Å, c = 7.5092 (5) Å, β = 90.93 (1)°, and two formula units per unit cell. VII crystallized in the monoclinic system, space group $P2_1/c$, with a = 6.787 (2) Å, b = 20.986 (3) Å, c = 16.825 (3) Å, β = 95.49 (2)°, and four formula units per unit cell. Refinement by full-matrix least squares gave final R factors of 0.039 for both systems. The copper centers in the binuclear cation in V are close to square planar with a bridging hydroxide angle of 126.0 (5)° and a Cu---Cu separation of 3.384 (2) Å. In VII the copper centers are considered to be distorted four-coordinate with axial contacts greater than 2.3 Å, a bridging hydroxide angle of 119.3 (2)°, and a Cu---Cu separation of 3.338 (1) Å. Variable-temperature magnetic studies on both complexes indicate strong antiferromagnetic exchange in both cations.

Introduction

Tetradentate phthalazine,[2-18] pyridazine,[3-5,19-23] and pyrazole ligands[3] have been shown to generate principally binuclear transition-metal complexes. Many of the copper(II) derivatives of the phthalazine systems have multiple bridges between the metal centers, including a hydroxide bridge, which is considered to be

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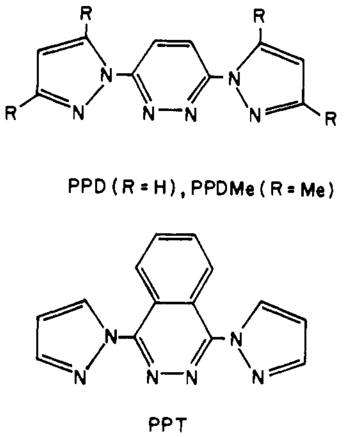

Figure 1. Structure of PPD (R = H), PPDMe (R = Me), and PPT.

the primary pathway for antiferromagnetic exchange, a feature which is characteristic of these systems.[6,14,16,17] The magnitude of the exchange integral has been shown to be a function of the hydroxide bridge angle, which can be varied by "tuning" the dimensions of the binuclear center with appropriately chosen anion bridges, the copper ion ground state, and also the chelate ring size.[14,16,17] The largest exchange observed so far ($-2J = 800$ cm^{-1}) was for the complex $Cu_2(MIP)(OH)Cl_3 \cdot 2H_2O$ (MIP = 1,4-bis(1-methyl-2-imidazolyl)phthalazine), which involved five-membered chelate rings and an oxygen (OH) bridge angle of 126.2°.[16] Complexes of the pyridylaminophthalazine ligands involving six-membered chelate rings and hydroxide bridges were observed to have much weaker exchange ($-2J < 540$ cm^{-1}) associated with smaller oxygen bridge angles (<116°).[14,17]

An approximately linear correlation between hydroxide bridge angle and exchange was observed for a series of phthalazine complexes involving $d_{x^2-y^2}$ copper ion ground states.[16] Other unrelated systems involving single hydroxide bridges, much larger bridge angles,[24,25] and $d_{x^2-y^2}$ copper ion ground states were shown to approximate this relationship, but for complexes with d_{z^2} ground states no such correlation was observed.[14,26]

Table I. Crystal Data

	$Cu_3C_{14}H_{21}Cl_5N_6O_3$ (V)	$Cu_2C_{14}H_{23}N_9O_{13}$ (VII)
cryst syst	monoclinic	monoclinic
space group	*Am*	$P2_1/c$
a, Å	7.4942 (4)	6.787 (2)
b, Å	20.418 (1)	20.986 (3)
c, Å	7.5091 (5)	16.825 (3)
β, deg	90.93 (1)	95.49 (2)
V, Å^3	1148.9	2385.34
Z	2	4
ρ(calcd), g cm^{-3}	1.99	1.797
μ, mm^{-1}	3.38	1.87
radiation; λ, Å	Mo Kα_1; 0.709 32	Mo Kα_1; 0.709 32
temp for data colln, °C	22	22
octants of data colld	$+h,+k,+l$ $-h,+k,+l$ $-h,-k,-l$ (partly)	$+h,+k,+l$ $-h,+k,+l$ $-h,-k,-l$ (partly)
equiv reflcns agreement	0.02	0.009
min an max transmission	0.52–0.65	0.69–0.76

Table II. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Cu_2(PPDMe)(OH)Cl_2][CuCl_3(H_2O)] \cdot H_2O$ (V)

atom	*x*	*y*	*z*	B_{iso},[a] Å^2
Cu(1)	0	0.8286 (5)	0	2.61 (4)
Cu(2)	0.04023 (24)	0	0.4140 (3)	2.52 (6)
Cl(1)	−0.2472 (3)	0.13458 (12)	0.0829 (4)	3.41 (9)
Cl(2)	0.2216 (3)	0.08184 (12)	0.3291 (4)	3.73 (11)
Cl(3)	−0.0939 (7)	0.0680 (3)	0.6064 (8)	3.77 (19)
O(1)	−0.0910 (12)	0	0.0687 (16)	3.5 (4)
O(2)	0.5763 (16)	0	0.2647 (21)	5.8 (7)
O(3)	−0.1654 (20)	0.0582 (7)	0.4450 (23)	3.9 (6)
N(1)	0.3057 (10)	0.1330 (3)	−0.1766 (11)	2.3 (3)
N(2)	0.1508 (10)	0.1553 (3)	−0.0959 (11)	2.4 (3)
N(3)	0.2031 (9)	0.0323 (3)	−0.1032 (10)	2.12 (24)
C(1)	0.3985 (11)	0.1849 (4)	−0.2466 (11)	2.5 (3)
C(2)	0.3028 (14)	0.2394 (4)	−0.2093 (14)	3.1 (4)
C(3)	0.1500 (12)	0.2195 (4)	−0.1169 (11)	2.3 (3)
C(4)	0.5662 (13)	0.1798 (5)	−0.3520 (17)	3.5 (4)
C(5)	−0.0001 (16)	0.2622 (5)	−0.0594 (16)	3.3 (4)
C(6)	0.3330 (11)	0.0651 (4)	−0.1792 (12)	2.2 (3)
C(7)	0.4827 (12)	0.0337 (4)	−0.2503 (14)	2.7 (3)
H(2)	0.327	0.285	−0.258	2.7
H(4A)	0.546	0.159	−0.446	2.4
H(4B)	0.615	0.221	−0.393	3.6
H(5A)	−0.044	0.247	0.031	2.5
H(5B)	0.045	0.294	−0.006	5.2
H(5C)	−0.051	0.291	−0.184	7.3

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

The importance of systems of this sort as structural/magnetic probes for the binuclear copper active sites in oxyhemocyanin and oxidase/oxygenase enzymes containing type III copper centers and the demonstrated catecholase activity of the phthalazine complexes $Cu_2(PAP)(OH)X_3$ (X = Cl, Br; PAP = 1,4-bis(2-pyridyl)aminophthalazine)[27] has led us to investigate the copper coordination chemistry of other binucleating diazine ligands, e.g. PPD (3,6-bis(1-pyrazolyl)pyridazine), PPDMe (3,6-bis(3,5-dimethyl-1-pyrazolyl)pyridazine) and PPT (1,4-bis(1-pyrazolyl)phthalazine) (Figure 1). These tetradentate, pyrazolyldiazine ligands form predominantly binuclear copper(II) complexes involving, in most cases, hydroxide bridges and exhibiting reduced magnetic moments. Full structural details are reported for the complex $[Cu_2(PPDMe)(OH)Cl_2][(CuCl_3(H_2O)] \cdot H_2O$ (V), which consists of a binuclear, hydroxide-bridged, copper(II) cation, with a hydroxide bridge angle of 126.0°, and an unusual mononuclear anion $[CuCl_3(H_2O)]^-$. The structural details for the complex $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3) \cdot H_2O$ (VII) are also reported, and in this system a hydroxide bridge angle of 119.3° is found. Limited variable-temperature magnetic data (80–200

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K) are reported for both V and VII, which indicate strong antiferromagnetic exchange between the copper(II) centers in the binuclear cations.

Experimental Section

Synthesis of Ligands. The syntheses of PPD[28] and PPDMe[29] have been reported previously. However the following procedure was found to be more effective for the production of these ligands and also PPT.

3,6-Bis(1-pyrazolyl)pyridazine (PPD). Pyrazole (6.8 g, 0.10 mol) was dissolved in dry THF (250 mL), and potassium metal (3.9 g, 0.10 mol), cut into small pieces, was added under nitrogen. The potassium disappeared on reaction with pyrazole, leaving a white suspension. 3,6-Dichloropyridazine (7.4 g, 0.05 mol) was dissolved in a minimal volume of dry THF under nitrogen and added to the suspension of potassium pyrazolide. The mixture was refluxed for 4 h, during which time the color changed from white to red-brown, and then added to 1 L of water, containing ice, with stirring. The remaining white solid was filtered, washed with water, dried, and recrystallized from DMF (yield 9.3 g (88%); mp 238–242 °C (lit.[28] 238–240 °C)).

3,6-Bis(3,5-dimethyl-1-pyrazolyl)pyridazine (PPDMe) (yield 80%; mp 165–167 °C (lit.[29] 166–167 °C)) and 1,4-bis(1-pyrazolyl)phthalazine (PPT), which was recrystallized from THF (yield 50%; mp 133–134 °C), were prepared similarly. Anal. Calcd for $C_{14}H_{10}N_6$ (PPT): C, 64.1; H, 3.82; N, 32.1. Found: C, 64.0; H, 3.78; N, 32.1. Mass spectrum, major mass peaks (m/e (relative intensity)): 262 (100), P, 235 (55), 195 (24), 168 (7), 128 (21), 102 (9). ^{1}H NMR ($CDCl_3$) (δ (relative intensity)): 6.55 (4) (pyrazole H_3), 7.93 (8) pyrazole $H_{2,4}$), 8.55 (4) (phthalazine H_B), 9.15 (4) (phthalazine H_α).

$[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII). PPDMe (0.50 g, 1.9 mmol) was dissolved in acetonitrile (50 mL) with warming and the solution filtered. A solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.90 g, 3.7 mmol) dissolved in water (10 mL) was filtered and then added and the resulting dark blue solution warmed on a steam bath until crystals began to form. A blue crystalline product was obtained on standing overnight, which was filtered and dried in air. All other complexes were prepared similarly by using various solvent combinations (ligand dissolved in organic solvent): I, II (DMF/H_2O), III, IV (CH_3CN/H_2O), V, VI, VIII (MeOH/H_2O; VI resulted by dissolving V in water and adding excess $ClO_4^-{}_{aq}$, IX, X, XIII, XIV (EtOH/H_2O), XI, XII (EtOH/EtOH). All complexes are listed in Table VIII.

Analyses. C, H, and N analyses were carried out by Canadian Microanalytical Service, Vancouver, Canada. Copper analyses were determined by atomic absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO_3 or aqua regia. Satisfactory C, H, N, and Cu analyses were obtained for all complexes reported.

Physical Measurements. Electronic spectra were recorded with a Cary 17 spectrometer and infrared spectra with a Perkin-Elmer Model 283 spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn Model No. #7600 Faraday Magnetic susceptibility system coupled to a Cahn gram electrobalance. Variable-temperature (80–200 K) magnetic data were obtained courtesy of B. Van der Griendt, Department of Chemistry, Gorlaeus Laboratories, State University Leiden, The Netherlands, using a PAR model 150A vibrating sample magnetometer. Nuclear magnetic resonance spectra were run as solutions in deuterochloroform on a Bruker WP80 spectrometer ($SiMe_4$ internal standard) and mass spectra were obtained on a V.G. Micromass 7070 HS spectrometer with a direct-insertion probe.

Crystallographic Data Collection and Refinement of the Structures. $[Cu_2(PPDMe)(OH)Cl_2][CuCl_3(H_2O)]\cdot H_2O$ (V). Crystals of V are deep green. The diffraction intensities of an approximately 0.2 × 0.15 × 0.13 mm crystal were collected with graphite-monochromatized Mo Kα radiation by using the $\theta/2\theta$ scan technique with profile analysis[30] to $2\theta_{max} = 65°$ on a Picker four-circle diffractometer with a PDP-8e computer. A total of 2801 reflections were measured, of which 2556 were unique, and 2007 reflections were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarization factors were applied, and absorption corrections were calculated. The cell parameters were obtained by least-squares refinement of the setting angles of 36 reflections with $2\theta > 45°$ (λ(Mo Kα_1) = 0.709 32 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 = 0.039 and R_w = 0.049 for the significant data (0.063 and 0.068 for all data) with unit weights. Only six H-atoms could be located from difference maps. Crystal data are given in Table I, and final atomic positional parameters and equivalent isotropic temperature factors are listed in Table II. All calculations were performed with the NRC PDP-8e system of programs,[31] adapted for the VAX 11/780 computer. Scattering factors were taken from ref 32. Anisotropic thermal parameters (Table III) and a listing of structure factors (Table IV) are included as supplementary material.

Table V. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII)[a]

atom	x	y	z	B_{eq}, Å^2
Cu(1)	0.25134 (12)	0.40088 (3)	0.32871 (4)	2.37 (4)
Cu(2)	0.35363 (13)	0.55142 (3)	0.38171 (4)	2.40 (4)
O(1)	0.3228 (6)	0.46332 (16)	0.41121 (20)	2.30 (18)
O(2)	0.3598 (6)	0.58115 (17)	0.49289 (21)	2.60 (20)
O(3)	0.5714 (6)	0.37229 (18)	0.30675 (24)	3.18 (21)
O(4)	0.8406 (9)	0.58505 (23)	0.1819 (3)	6.6 (3)
N(1)	0.0415 (10)	0.3342 (3)	0.4221 (3)	3.3 (3)
O(11)	0.2193 (7)	0.33189 (20)	0.4062 (3)	3.26 (23)
O(12)	−0.0662 (7)	0.37854 (24)	0.3938 (3)	4.8 (3)
O(13)	−0.0247 (9)	0.29254 (24)	0.4637 (3)	6.1 (3)
N(2)	0.6973 (11)	0.4315 (4)	0.1069 (4)	5.0 (4)
O(21)	0.7104 (10)	0.4364 (3)	0.1795 (3)	8.3 (4)
O(22)	0.6048 (11)	0.3920 (3)	0.0716 (5)	11.5 (6)
O(23)	0.7855 (9)	0.4729 (3)	0.0724 (3)	6.8 (4)
N(3)	−0.1335 (12)	0.5540 (4)	0.3937 (4)	4.8 (4)
O(31)	−0.2877 (9)	0.5324 (3)	0.3799 (5)	11.7 (6)
O(32)	−0.0126 (10)	0.5709 (3)	0.3537 (4)	8.9 (4)
O(33)	−0.0829 (14)	0.5585 (4)	0.4666 (4)	14.1 (7)
N(4)	0.1721 (7)	0.38761 (23)	0.1605 (3)	2.36 (23)
N(5)	0.1520 (8)	0.35422 (23)	0.2297 (3)	2.52 (24)
N(6)	0.2654 (7)	0.46721 (22)	0.2463 (3)	2.15 (23)
N(7)	0.3234 (7)	0.52648 (22)	0.2667 (3)	2.10 (24)
N(8)	0.3993 (8)	0.63361 (22)	0.3278 (3)	2.39 (24)
N(9)	0.3947 (8)	0.62895 (23)	0.2455 (3)	2.34 (23)
C(1)	0.1201 (10)	0.3510 (3)	0.0941 (4)	3.0 (3)
C(2)	0.0672 (11)	0.2940 (3)	0.1225 (4)	3.4 (3)
C(3)	0.0861 (10)	0.2969 (3)	0.2056 (4)	2.9 (3)
C(4)	0.1343 (18)	0.3724 (5)	0.0100 (5)	4.6 (5)
C(5)	0.0441 (15)	0.2459 (4)	0.2628 (5)	4.1 (4)
C(6)	0.2357 (9)	0.4511 (3)	0.1708 (3)	2.2 (3)
C(7)	0.2646 (10)	0.4947 (3)	0.1101 (3)	3.0 (3)
C(8)	0.3217 (10)	0.5550 (3)	0.1308 (3)	2.7 (3)
C(9)	0.3474 (9)	0.5698 (3)	0.2124 (3)	2.3 (3)
C(10)	0.4350 (10)	0.6874 (3)	0.2133 (4)	2.8 (3)
C(11)	0.4656 (10)	0.7283 (3)	0.2746 (4)	2.9 (3)
C(12)	0.4438 (10)	0.6941 (3)	0.3451 (4)	2.6 (3)
C(13)	0.4605 (13)	0.7192 (4)	0.4294 (5)	3.8 (4)
C(14)	0.4417 (16)	0.6986 (4)	0.1258 (5)	4.2 (5)
H(2)	0.02191	0.25552	0.08829	3.96
H(7)	0.24402	0.48172	0.05152	3.67
H(8)	0.34838	0.58791	0.08896	3.37
H(11)	0.50152	0.77512	0.27075	3.37
H(41)	0.103 (11)	0.345 (3)	−0.018 (4)	5.2 (23)
H(42)	0.047 (10)	0.403 (3)	−0.003 (4)	3.6 (19)
H(43)	0.318 (16)	0.380 (5)	0.001 (6)	15.7 (40)
H(51)	0.136 (11)	0.241 (3)	0.301 (4)	6.1 (24)
H(52)	−0.108 (12)	0.254 (4)	0.288 (5)	9.0 (26)
H(53)	0.03697	0.20375	0.23590	4.45
H(131)	0.373 (11)	0.699 (3)	0.464 (4)	7.3 (25)
N(132)	0.470 (11)	0.766 (3)	0.436 (4)	6.7 (21)
H(133)	0.60389	0.70697	0.45007	4.17
H(141)	0.480 (10)	0.733 (3)	0.125 (4)	3.8 (20)
H(142)	0.561 (11)	0.670 (3)	0.104 (4)	7.4 (25)
H(143)	0.308 (10)	0.687 (3)	0.094 (4)	6.0 (21)

[a] Hydrogen atoms for which esd's are not given were not refined. B_{eq} is the mean of the principal axes of the thermal ellipsoid.

$[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII). Crystals of VII are blue. The diffraction intensities of an approximately 0.25 × 0.2 × 0.15 mm crystal were collected with graphite-monochromatized Mo Kα radiation generated at 50 KV and 16 mA by using the $\theta/2\theta$ scan technique and profile analysis with a Picker four-circle diffractometer and PDP-8e computer.[30] The data were collected to $2\theta = 50°$, giving a total

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Table VIII. Spectral and Magnetic Data

no.	compd	IR, cm^{-1}	d–d [shoulder],[a] cm^{-1}	μ_{eff},[b] μ_B
I	$Cu_2(PPD)(OH)Cl_3 \cdot 2H_2O$	3550 (OH), 3400, 3350 (H_2O), 340, 323 (Cu–Cl)	14 500	0.55
II	$Cu_2(PPD)(OH)Br_3 \cdot 1.5H_2O$	3520 sh (OH), 3430, 3380 (H_2O), 260 (Cu–Br)	16 700, 19 000	c
III	$Cu(PPD)_2(NO_3)_2$	1763, 1748 ($\nu_1 + \nu_4$, NO_3^-)	15 800	1.83
IV	$Cu(PPD)_2(ClO_4)_2 \cdot 0.5H_2O$	3450 (H_2O), 1130, 1105, 1070, 1040 (ClO_4^-)	15 800	1.84
V	$[Cu_2(PPDMe)(OH)Cl_2][CuCl_3(H_2O)] \cdot H_2O$	3530 (OH), 3400 (H_2O), 315, 305, 290 (Cu–Cl)	[10 900], 14 700, [16 400]	1.03
VI	$[Cu_2(PPDMe)(OH)Cl_2] \cdot ClO_4$	3570 (OH), 1100 (ClO_4^-)	15 900	0.26
VII	$[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2]NO_3 \cdot H_2O$	3540 (OH), 3490, 3280 (H_2O), 1781, 1761, 1756, 1742 ($\nu_1 + \nu_4$, NO_3^-)	16 000	0.55
VIII	$Cu(PPDMe)_2(ClO_4)_2 \cdot H_2O$	3370 (H_2O), 1100 (ClO_4^-)	11 100, 13 300	1.98
IX	$Cu_2(PPT)(OH)Cl_3 \cdot 2H_2O$	3500 (OH), 3420, 3300 (H_2O), 303, 288, 280 (Cu–Cl)	14 800	0.54
X	$Cu_2(PPT)(OH)Br_3 \cdot H_2O \cdot 0.25EtOH$	3520 (OH), 3440, 3350 (H_2O), 268, 239 (Cu–Br)	15 400	0.36
XI	$Cu_2(PPT)Cl_4 \cdot 4H_2O$	3400 (H_2O), 340, 330, 305 (Cu–Cl)	[11 500], 14 300	1.38
XII	$Cu_2(PPT)Br_4 \cdot 3H_2O$	3420 (H_2O), 270, 240 (Cu–Br)	17 800	0.93
XIII	$Cu_2(PPT)(OH)(NO_3)_3 \cdot H_2O$	3520 (OH), 3380 (H_2O), 1760, 1752, 1730 ($\nu_1 + \nu_4$, NO_3^-)	[12 300], 15 400	0.74
XIV	$Cu(PPT)_2(ClO_4)_2 \cdot 1.5EtOH \cdot H_2O$	1100 (ClO_4^-)	17 400	1.84

[a] Mull transmittance. [b] Room temperature. [c] Diamagnetic.

of 5340 valid measurements of which 4210 are unique and 3142 reflections are considered to be significant at the $2.5\sigma(I_{net})$ level. Lorentz and polarization factors were applied, but no absorption correction was calculated ($\mu = 1.87$ mm^{-1}). The cell parameters were obtained by the least-squares refinement of the setting angles of 44 reflections with $2\theta > 40°$. Crystal and other data are given in Table I.

The structure was solved by the application of MULTAN.[33] The H atomic positions of PPDMe were calculated; 10 of the Me group H atoms were located from *D* maps and the remaining 2 calculated. Attempts to locate the H atoms of H_2O and OH were unsuccessful. The structure was refined with full-matrix least squares and the final agreement factors are $R_F = 0.050$ and $R_w = 0.039$ with counting statistics weights and $R_F = 0.071$ and $R_w = 0.040$, including insignificant reflections. The atomic positional parameters and equivalent isotropic temperature factors are listed in Table V. All calculations were performed by using the NRC PDP-8e system of programs[31] adapted for a VAX 11/780 computer. Scattering factors were taken from ref 32. Anisotropic thermal parameters (Table VI) and structure factors (Table VII) are included as supplementary material.

Results and Discussion

When water is a major solvent component in the synthesis of copper chloride and bromide complexes of PPD, PPDMe, and PPT, hydroxide-bridged binuclear derivatives are produced. These are characterized by the appearance of generally sharp absorptions in the infrared above 3500 cm^{-1} (Table VIII). In some cases (XI, XII), if the water content is minimized, binuclear tetrahalide derivatives are produced. This phenomenon has also been observed with complexes of other tetradentate pyridazine and phthalazine ligands.[16,19-23]

A binuclear nitrate derivative of PPD could not be synthesized, but with PPDMe and PPT hydroxide-bridged nitrate species were produced. Binuclear complexes could not be synthesized with copper perchlorate, and in all cases mononuclear derivatives were obtained. This trend of the formation of predominantly binuclear derivatives with normally coordinating anions and mononuclear species with poorly coordinating anions reflects the obvious ligand field requirement of the copper centers in these systems. It was noticeable in the syntheses of some complexes, especially of PPD, that if equilibrium conditions were unfavorable for complex formation, unreacted ligand began to crystallize from the reaction mixture. Complex formation was achieved by the choice of an appropriate solvent system and heating of the reaction mixture until product began to form.

The mononuclear complexes appear to contain two bidentate ligands, which are presumably bound via one pyrazole and one pyridazine or phthalazine nitrogen. This situation has been observed before with other tetradentate phthalazine ligands[10,16] and is usually characterized by the appearance of a more complex CN stretching region in the infrared than for the more symmetrical, binuclear derivatives. For III and IV three bands are observed in this region while for I and II only two are evident. A similar situation is observed for the other mononuclear bis(ligand) derivatives.

The splitting of the nitrate combination bands[34] in the infrared spectrum of III suggests the presence of monodentate nitrate and a six-coordinate derivative, in keeping with electronic spectral data. IV exhibits a ν_3 perchlorate absorption in the infrared, which is split into several major components, suggesting coordinated perchlorate and a six-coordinate complex. III and IV appear to be structurally similar with a tetragonally distorted six-coordinate stereochemistry. In contrast VIII has ionic perchlorate, and judging by the low-energy visible absorption, it probably has a distorted tetrahedral structure. The presence of the methyl groups on the pyrazole ring in PPDMe may result in enough of a steric effect to generate this tetrahedral distortion. For XIV ionic perchlorate and a higher energy visible band suggest a square-planar derivative. The higher magnetic moment associated with VIII is indicative of a system with a dominant T ground term.

The apparently trinuclear complex V in fact has a rather unusual structural arrangement involving a hydroxide-bridged binuclear cation with a distorted tetrahedral species, $[CuCl_3(H_2O)]^-$, as the counteranion (see structure description). The binuclear cation is an essentially planar species with distorted four-coordinate square-planar metal centers. The oxygen bridge angle at hydroxide is 126.0°, and the metal–metal separation is 3.384 Å. The rich visible absorption observed for this species (Table VIII) is thus associated with two differing copper centers, and the room-temperature magnetic moment thus becomes the average of a spin-coupled pair and an essentially spin-free copper center in the ion $[CuCl_3(H_2O)]^-$.

Complex VI probably contains the same hydroxide-bridged binuclear cation present in V and is characterized by a single visible band at 15 900 cm^{-1}. This band corresponds closely with one component of the visible absorption envelope for V, estimated at 16 400 cm^{-1}. The other two lower energy absorptions in V are therefore associated with the distorted tetrahedral anion $[CuCl_3(H_2O)]^-$. The analogous nitrate complex VII is again a hydroxide-bridged species but with a smaller oxygen bridge angle of 119.3° and a copper–copper separation of 3.338 Å. This complex exhibits four discernible nitrate combination band ($\nu_1 + \nu_4$) absorptions,[34] indicative of more than one different type of nitrate group. The X-ray structure reveals an ionic nitrate, an intermolecular bridging nitrate, and a "pseudo" bidentate nitrate. Absorptions at 1756 cm^{-1} and two bands at 1761 and 1742 cm^{-1} can be associated with ionic and bidentate nitrate respectively, while the high-energy band (1781 cm^{-1}) is assigned to the intermolecular bridging nitrate. A high-energy combination band at 1784 cm^{-1} was associated with a bidentate intramolecular nitrate

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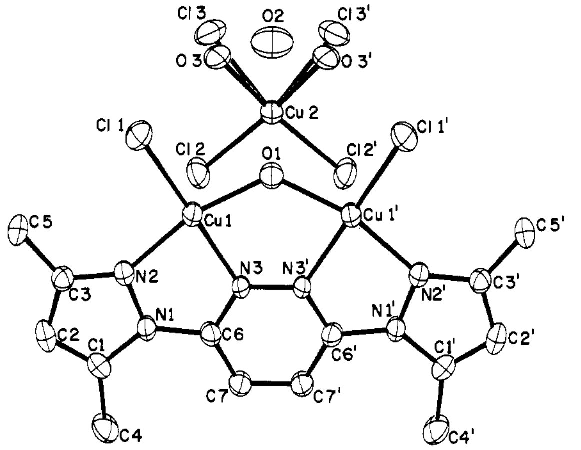

Figure 2. Structural representation of $[Cu_2(PPDMe)(OH)Cl_2][CuCl_3(H_2O)]\cdot H_2O$ (V) with hydrogen atoms omitted for clarity. The primed atoms are related to the unprimed atoms by the transformation *x*, −*y*, *z*.

Table IX. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(PPDMe)(OH)Cl_2][CuCl_3(H_2O)]\cdot H_2O$ (V)[a]

Cu(1)–Cu(1)′	3.384 (2)	Cu(2)–Cl(2)	2.252 (3)
Cu(1)–Cu(2)	3.548 (2)	Cu(2)–Cl(3)	2.252 (5)
Cu(1)–O(1)	1.898 (4)	Cu(2)–O(3)	1.963 (13)
Cu(1)–N(3)	2.006 (6)	Cu(1)–Cl(2)	2.955 (5)
Cu(1)–N(2)	2.003 (7)	Cu(2)–O(1)	2.758 (4)
Cu(1)–Cl(1)	2.229 (2)		
Cu(1)–O(1)–Cu(1)′	126.0 (5)	Cl(2)–Cu(2)–Cl(3)	90.1 (2)
Cu(1)–O(1)–Cu(2)	97.5 (3)	Cl(2)–Cu(2)–Cl(3)′	156.4 (2)
O(1)–Cu(1)–N(3)	85.6 (3)	Cl(2)–Cu(2)–O(3)	93.6 (4)
N(3)–Cu(1)–N(2)	78.8 (3)	Cl(2)–Cu(2)–O(3)′	164.0 (6)
N(2)–Cu(1)–Cl(1)	103.1 (2)	Cl(3)–Cu(2)–Cl(3)′	76.2 (2)
Cl(1)–Cu(1)–O(1)	92.4 (2)	Cl(3)–Cu(2)–O(3)	36.0 (6)
O(1)–Cu(1)–N(2)	164.4 (3)	Cl(3)–Cu(2)–O(3)′	86.4 (4)
N(3)–Cu(1)–Cl(1)	172.3 (2)	O(3)–Cu(2)–O(3)′	74.5 (6)
Cl(2)–Cu(2)–Cl(2)′	95.8 (1)		

[a] Esd's are given in parentheses.

bridge in a related binuclear phthalazine complex[17].

The hydroxy-bridged species, I, II, IX, X, and XIII, appear to involve binuclear centers bridged by just the diazine (N–N) and a hydroxide, while the species XI and XII probably involve a diazine (N–N) and a halogen bridge. Structurally these systems will probably resemble related complexes involving tetradentate phthalazine and pyridazine ligands with five-membered chelate rings.[16,19–23]

Description of the Structures of $[Cu_2(PPDMe)(OH)Cl_2][CuCl_3(H_2O)]\cdot H_2O$ (V) and $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII). The structure of V is shown in Figure 2, and interatomic distances and angles relevant to the copper coordination spheres are given in Table IX. The binuclear cation in V consists of an essentially planar species with two four-coordinate metal centers bound to the tetradentate binucleating ligand via atoms N(2), N(3), N(3)′, and N(2)′. A crystallographic mirror plane bisects the cation, through the oxygen bridge (O(1)) and the pyridazine ring, and the anion. The two pyrazole rings are coplanar and canted by 6.2° with respect to the pyridazine ring. The two copper centers are bridged by the diazine fragment of the pyridazine ring (N(3)–N(3)′) and an oxygen (O(1)). Although a hydrogen atom could not be located on O(1), other data, including an infrared band at 3530 cm^{-1}, leave little doubt as to the identity of this bridge as hydroxide. The copper centers are essentially planar with a displacement of Cu(1) of 0.103 (4) Å with respect to the mean plane of the N_2ClO entity. A large angle of 126.0° is observed at the oxygen bridge with a copper–copper separation of 3.384 Å.

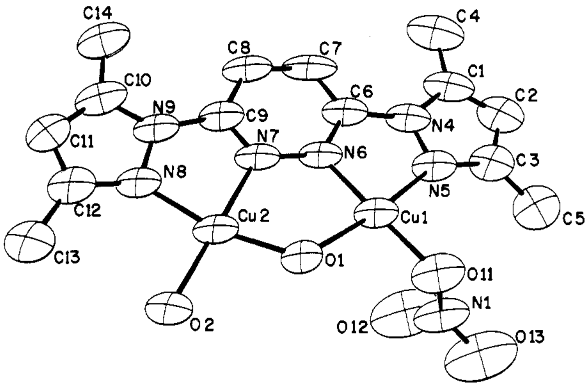

Figure 3. View of the binuclear cation in $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII) with hydrogen atoms omitted for clarity.

Table XI. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII)[a]

Cu(1)–O(1)	1.936 (3)	Cu(2)–O(1)	1.931 (3)
Cu(1)–O(11)	1.973 (4)	Cu(2)–O(2)	1.969 (4)
Cu(1)–N(5)	1.993 (5)	Cu(2)–N(7)	1.995 (4)
Cu(1)–N(6)	1.973 (4)	Cu(2)–N(8)	1.986 (5)
Cu(1)–O(12)	2.553 (5)	Cu(2)–O(32)	2.518 (6)
Cu(1)–O(3)	2.317 (4)	Cu(2)–O(31′)	2.470 (7)
Cu(1)–Cu(2)	3.338 (1)		
O(11)–Cu(1)–O(1)	93.4 (2)	O(2)–Cu(2)–O(1)	93.0 (2)
O(11)–Cu(1)–N(5)	98.1 (2)	O(2)–Cu(2)–N(8)	99.7 (2)
N(5)–Cu(1)–N(6)	78.1 (2)	N(8)–Cu(2)–N(7)	78.0 (2)
N(6)–Cu(1)–O(1)	90.0 (2)	N(7)–Cu(2)–O(1)	89.7 (2)
O(11)–Cu(1)–N(6)	175.6 (2)	O(2)–Cu(2)–N(7)	174.4 (2)
N(5)–Cu(1)–O(1)	166.6 (2)	N(8)–Cu(2)–O(1)	167.0 (2)
O(12)–Cu(1)–O(3)	149.7 (2)	O(32)–Cu(2)–O(31′)	168.6 (3)
N(1)–O(11)	1.262 (8)	O(11)–N(1)–O(12)	118.9 (5)
N(1)–O(12)	1.249 (8)	O(12)–N(1)–O(13)	120.9 (6)
N(1)–O(13)	1.231 (8)	O(13)–N(1)–O(11)	120.2 (6)
		Cu(1)–O(11)–N(1)	106.3 (4)
		Cu(1)–O(1)–Cu(2)	119.3 (2)

[a] Esd's are given in parentheses.

The oxygen bridge angle and copper–copper separation in V compare closely with values of 126.5°, 3.376 Å and 128.1°, 3.398 Å for the complexes $[Cu_2L(OH)Cl_3(H_2O)]$ and $[Cu_2L(OH)Br_3]_n$, respectively, where L is the related pyridazine ligand 3,6-bis(2-pyridyl)pyridazine,[20,23] and also with values of 126.3° and 3.425 Å found for the complex $[Cu_2(MIP)(OH)Cl_3(H_2O)]H_2O$ (MIP = 1,4-bis(1-methyl-2-imidazolyl)phthalazine).[16] In all these systems each copper center is part of a five-membered chelate ring involving one diazine nitrogen atom and one nitrogen atom from a peripheral donor group. The transition from a similar six-membered chelate ring, observed in several pyridylaminophthalazine complexes, to five-membered rings results in significant expansion of the binuclear centers, and increases in Cu–O–Cu bridge angles of as much as 26° are observed.[12,14,16,17]

The anion $[CuCl_3(H_2O)]^-$, found in V, represents an unusual and to our knowledge previously unreported species, which occupies a symmetric position in the crystal lattice with the chlorine atoms Cl(2) and Cl(2)′ lying above the copper atoms in the binuclear cation. The triangular framework of the three copper atoms can be considered to be linked by the chlorine atoms Cl(2) and Cl(2)′ and oxygen O(1) but the copper–chlorine separation (Cu(1)–Cl(2)) of 2.955 Å and copper–oxygen separation (Cu(2)–O(1)) of 2.758 Å indicates little, if any, interaction. The anion structure is disordered with two chlorine atoms (Cl(2), Cl(2)′), two oxygen half-atoms (O(3), O(3)′) and two chlorine half-atoms (Cl(3), Cl(3)′) bound to Cu(2). A reasonable way to consider this ion would be as an average of two flattened tetrahedra Cu(2)-Cl(2)-Cl(2)′-O(3)-Cl(3)′ and Cu(2)-Cl(2)-Cl(2)′-O(3)′-Cl(3). The fact that Cl(2) and Cl(2)′ are not disordered indicates the possibility of some interaction, albeit small, with the two copper centers in the binuclear cation.

Figure 3 illustrates a structural representation of VII, and appropriate interatomic distances and angles relevant to the copper

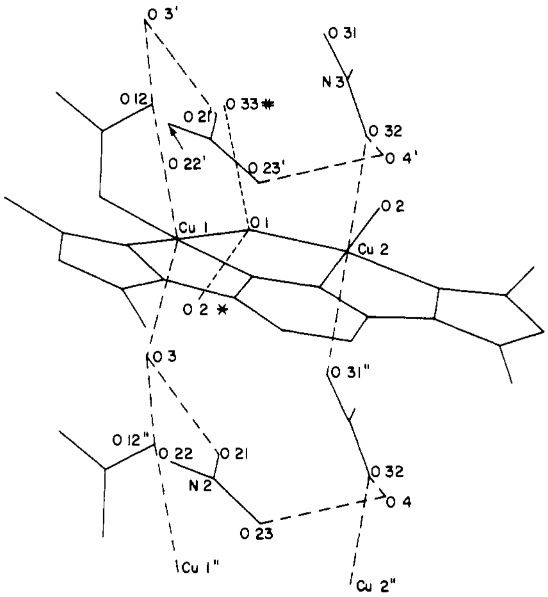

Figure 4. Molecular packing arrangement in $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII), showing chains parallel to the *a* axis, and the cross-linking between the chains.

coordination spheres are given in Table XI. The two copper(II) centers are bridged by the pyridazine group (N(6)–N(7)) and a hydroxide. Although a hydrogen atom could not be located on O(1), other data, including an infrared absorption at 3540 cm^{-1}, leave little doubt as to the identity of this bridge group as hydroxide. The molecule is essentially planar; the distance from Cu(1) to the mean plane of O(1), O(11), N(5), and N(6) is –0.079 (3) Å while the distance from Cu(2) to the mean plane of O(1), O(2), N(7), and N(8) is 0.014 (2) Å. Each copper center has four relatively short bonding interactions (<2 Å) and two longer contacts. Defining the coordination number of each copper may be a matter for personal choice, but certainly in terms of strongly bound ligands four-coordination would be appropriate. While oxygen O(11) is bound to Cu(1), oxygen O(12) at a distance of 2.55 Å may also be considered to have a weak interaction with the copper center. It has been suggested that in unsymmetrically coordinated bidentate nitrate groups the difference between the Cu–O bond lengths, involving the two coordinated oxygen atoms, falls in the range 0.2–0.7 Å.[35] In this case the difference is less than 0.6 Å. In another example of a nitrato complex, where, even though the Cu–O bond length difference was 0.84 Å, other structural and spectral evidence suggested a weak interaction involving a distant nitrate oxygen atom.[36] Perhaps, therefore, both copper centers should be regarded as severely tetragonally distorted octahedra.

The binuclear center is characterized by a metal–metal separation of 3.338 Å, an oxygen bridge angle of 119.3°, and Cu–O(1) separations of 1.936 and 1.931 Å. The oxygen bridge angle is somewhat smaller than those observed in V, in related pyridyl pyridazine complexes (122–128°)[19-23] and in the complex $[Cu_2(MIP)(OH)Cl_3(H_2O)]H_2O$ (126.3°).[16] The molecules of VII are stacked together in the lattice, as shown in Figure 4. There are two chains of contacts, O(12)–Cu(1)–O(3)–O(12″) and O(31)–N(3)–O(32)–Cu(2)–O(31″), which are roughly parallel to the *a* axis. The molecules in the stack formed by these chains are cross-linked, via contacts at O(1), to the molecules in another similar stack. There is also a cross-like between the chains themselves, via hydrogen bonds through O(3)–O(21)–N(2)–O(23)–O(4)–O(32″). Relevant distances and angles are given in Table XII.

The symmetric nature of the cation in V contrasts with that observed for VII in which two nitrate groups are weakly associated with one copper center and one with the other. The copper–copper separation in V is slightly larger than that in VII, but the oxygen bridge angle of 126.0° is very much larger than that in VII (119.3°). The diazine (N–N) bond length in V (1.317 Å) is somewhat shorter than that in VII (1.339 Å), but slightly larger Cu–N–N (diazine) angles offset this difference, giving rise to the larger copper–copper separation in V. The major difference between the binuclear centres (Cu_2N_2O) rests with the Cu–O(bridge) bond lengths and the O(bridge)–Cu–N angles. In V significantly shorter Cu–O(bridge) bond lengths occur with O(bridge)–Cu–N angles that are in excess of 4° smaller than in VII. This leads to a much larger oxygen bridge angle in V. A chemical rationale for this difference can be advanced by considering the fact that chlorine atoms occupy the fourth in-plane coordination sites in V, while a water molecule and a nitrate group exist in these positions in VII. The electronegative chlorine atoms can be considered to enhance the Lewis acidity of the copper centers, thus favoring the formation of shorter Cu–O(bridge) bonds in V.

Table XII. Intermolecular Distances (Å) and Angles (deg) Relevant to the Stacking Arrangement of Molecules in $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2](NO_3)\cdot H_2O$ (VII)[a]

O(12)–Cu(1)	2.553 (5)	O(3′)–O(12)–Cu(1)	122.0 (2)
Cu(1)–O(3)	2.317 (4)	O(12)–Cu(1)–O(3)	149.7 (2)
O(3)–O(12″)	2.743 (6)	Cu(1)–O(3)–O(12)	135.1 (2)
N(3)–O(32)	1.165 (9)	N(3)–O(32)–Cu(2)	125.4 (6)
O(32)–Cu(2)	2.518 (6)	O(32)–Cu(2)–O(31″)	168.6 (3)
Cu(2)–O(31″)	2.470 (7)	Cu(2)–O(31″)–N(3″)	144.9 (7)
O(31″)–N(3″)	1.143 (10)		
O(33†)–O(1)	2.780 (9)	O(33†)–O(1)–O(2*)	89.5 (2)
O(1)–O(2*)	2.729 (5)		
O(3)–O(21)	2.769 (7)	O(12″)–O(3)–O(21)	92.0 (2)
O(23)–O(4)	2.990 (8)	O(23)–O(4)–O(32″)	122.0 (2)
O(4)–O(32″)	2.982 (8)		

[a] Symmetry code: (none) *x*, *y*, *z*; (′) –*x*, *y*, *z*; (″) 1 + *x*, *y*, *z*; (*) –*x*, –*y*, –*z*; (†) 1 + *x*, –*y*, –*z*.

Magnetism. All of the binuclear complexes have reduced room-temperature magnetic moments indicative of antiferromagnetic exchange between the copper(II) centers. The hydroxide-bridged species have very low moments (<0.74 μ_B), and in once case, $Cu_2(PPD)(OH)Br_3\cdot 1.5H_2O$ is diamagnetic. XI and XII are clearly not hydroxide-bridge species but because of reduced room-temperature moments are likely to be halogen bridged. The mononuclear derivatives are characterized by having "normal" room-temperature moments indicative of *non*exchanged centers. The trinuclear derivative, V, which has been shown to consist of a binuclear center and an isolated mononuclear center, has a room-temperature moment of 1.03 μ_B. The Cu(1)–Cl(2) distance (2.955 Å) and the Cu(2)–O(1) distance (2.758 Å) are too large to consider the possibility of any spin exchange between the binuclear center and Cu(2), and so the magnetism can be explained in terms of the contribution of two isolated centers. Variable-temperature magnetic measurements were carried out on powdered samples of V and VII in the temperature range 80–200 K. The data for V appear to follow the Curie law fairly closely, with an extrapolated intercept of the linear reciprocal susceptibility/temperature plot of close to absolute zero, indicating that the binuclear center contributes little to the total susceptibility of the system. It was not possible to fit the experimental data to the Van Vleck equation[37] for exchange-coupled pairs of copper(II) ions with meaningful values of the variables *g* and $-2J$. Assuming a magnetic moment at 200 K of 1.8 μ_B for the anion $[CuCl_3(H_2O)]^-$ the calculated value for the exchange-coupled cation is <0.3 μ_B, indicating a very strongly coupled binuclear center. This value agrees closely with that observed for the complex $Cu_2(PPDMe)(OH)Cl_2\cdot ClO_4$ (VI), which appears to have the same binuclear cation. Variable-temperature data for VII were fitted

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to the Van Vleck equation with $g = 2.0 \pm 0.1$ and $-2J = 750 \pm 50$ cm^{-1}. The large scatter in the data obtained for this system and the narrow range of temperature over which measurements were made place large errors on the values of g and $-2J$, but the results clearly indicate a strongly antiferromagnetically coupled complex.

The fact that $Cu_2(PPD)(OH)Br_3 \cdot 1.5H_2O$ is diamagnetic at room temperature is unusual (repeated measurements with large samples gave the same result) and suggests very large antiferromagnetic exchange. Other examples of binuclear copper(II) complexes that are diamagnetic are rare and usually involve 1,3-azide or O-carbonate bridges.[38–44] In the carbonate-bridged systems a single oxygen atom bridges the two copper centers, and Cu–O–Cu angles of greater than 172° lead to room-temperature diamagnetism. A linear relationship between the exchange integral ($-2J$) and Cu–O–Cu bridge angle has been demonstrated for a series of related dihydroxo-bridged copper(II) systems[45] and also for a series of related monohydroxo-bridged copper(II) systems involving $d_{x^2-y^2}$ ground states with exchange increasing with bridge angle.[16,17] Such a relationship has, however, not been demonstrated with other oxygen bridge groups, and although the carbonate-bridged species are diamagnetic, it is not clear whether such large oxygen bridge angles are necessary to cause complete spin pairing at room temperature. An extrapolation of a linear plot of room-temperature magnetic moment against hydroxide bridge angle for a related series of monohydroxo-bridge copper(II) complexes with $d_{x^2-y^2}$ copper ion ground states[16,17] suggests that an angle of about 145° should lead to room-temperature diamagnetism. It is of interest to note that oxyhemocyanin is "diamagnetic" over the temperature range 5–260 K[46,47] ($-2J >$ 1100–1250 cm^{-1}) and appears to have a single atom, endogenous bridge (probably an oxygen atom) according to EXAFS and other studies. Assuming reasonable values for the Cu–OR(bridge) (1.90 Å) and Cu–Cu (3.65 Å) separations in oxyhemocyanin a Cu–O–Cu angle of ~145° would result by simple trigonometry.[48]

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Supplementary Material Available: Listings of anisotropic thermal parameters for V and VII (Tables III and VI), observed and calculated structure factor amplitudes for V and VII (Tables IV and VII), bond length and bond angle data pertaining to the ligand in V (Table X), bond length and bond angle data pertaining to the ligand and distant nitrate groups in VII (Table XIII), and least-squares-plane calculations for V and VII (Table XIV) (49 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Study of 2,4-Disubstituted 1,3-Diaryl-1,3,2,4-diazadiphosphetidines

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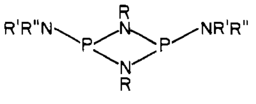
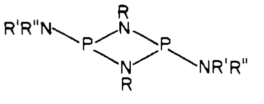
Reactions of *cis*-$[(C_6H_5N)PCl]_2$ (**5**) with $(C_6H_5)_2NH$, $(n\text{-}C_4H_9)_2NH$, or $i\text{-}C_3H_7NH_2$ yield the new *trans*-1,3,2,4-diazadiphosphetidines $[(C_6H_5N)PN(C_6H_5)_2]_2$ (**6**), $[(C_6H_5N)PN(n\text{-}C_4H_9)_2]_2$ (**10**), and $[(C_6H_5N)PNH(i\text{-}C_3H_7)]_2$ (**12**), respectively. **6**, **10**, and **12** have been characterized in solution by spectral data. **5** and **6** have been characterized by single-crystal X-ray crystallographic analysis. Lattice parameters and space group information are as follows. For **5**: $a = 16.034$ (5) Å, $b = 11.405$ (3) Å, $c = 7.826$ (2) Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, $Cmc2_1$, $Z = 4$. For **6**: $a = 7.795$ (3) Å, $b = 13.533$ (8) Å, $c = 17.046$ (7) Å, $\beta = 103.12$ (3)°, monoclinic, $P2_1/c$, $Z = 2$. Structures were solved and refined by direct methods to (**5**) $R = 0.061$ and $R_w = 0.077$ for 390 independent reflections and (**6**) $R = 0.097$ and $R_w = 0.108$ for 801 independent reflections. **5** is a cis isomer with a planar P_2N_2 ring (approximate C_{2v} molecular symmetry). **6** is a trans isomer (C_i molecular symmetry). **5**, **6**, **10**, and **12** are obtained in their thermodynamically favored isomeric forms. From **6**–$C_6H_5NH_2$ and $[(C_6H_5)_2N]_2PCl$–$C_6H_5NH_2$ [in the presence of $(C_2H_5)_3N$] reactions the thermodynamically stable *cis*-$[(C_6H_5N)_2P_2N(C_6H_5)_2(NHC_6H_5)]$ is obtained and characterized. *cis*-$[(C_6H_5N)_2P_2(Cl)N(C_6H_5)_2]$ is characterized tentatively as the major product of the reaction of a deficiency of $(C_6H_5)_2NH$ with **5**. Relative stabilities of cis and trans isomers in *N*(ring)-aryl-substituted diazadiphosphetidines and the factors that influence these are discussed.

Introduction

Structural properties of phosphorus(III) 1,3,2,4-diazadiphosphetidines,[2] especially 2,4-diamino-1,3-dialkyl-substituted species (**1**; R = alkyl), have received considerable recent attention.



1a



1b

Cis–trans isomerism,[3–24] rotation around *exo*-P–N bonds,[20–22,25–27] and the factors that affect relative isomer stability have been

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(2) The 1,3,2,4-diazadiphosphetidine nomenclature system advocated by *Chem. Abstr.* and diazadiphosphetidine are used synonomously throughout this paper.

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