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Variable Antiferromagnetic Exchange in a Series of Binuclear Copper(II) Complexes of Tetradentate (N_4) and Hexadentate (N_6) Diazine Ligands. Magnetism versus Structure, Bridging and Terminal Ligand Groups, and Chelate Ring Size. Crystal and Molecular Structure of [μ-1,4-Bis((6-methylpyrid-2-yl)amino)phthalazine](μ-hydroxo)(μ-nitrato-*O*)-bis(nitrato)dicopper(II)-0.5-Water, $Cu_2C_{20}H_{19}N_9O_{10}\cdot 0.5H_2O$†

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The spin exchange in a series of binuclear copper(II) complexes of polyfunctional phthalazine and pyridazine ligands, with predominantly hydroxide-bridged binuclear centers, is examined and related to structural features including copper ion stereochemistry, chelate ring size, hydroxide bridge angle, the size of non-hydroxide bridge groups, and the polarizing nature of certain terminally bound ligands. Chloro-bridged complexes exhibit small exchange integrals ($-2J$ = 55–131 cm^{-1}), and much larger exchange integrals are observed for the hydroxo-bridged compounds ($-2J$ = 190–1304 cm^{-1}). The crystal and molecular structure of [Cu_2(PAP6Me)(OH)(NO_3)$_3$]·0.5H_2O is reported (PAP6Me = 1,4-bis((6-methylpyrid-2-yl)amino)phthalazine). This complex crystallizes in the monoclinic system, space group $P2_1/a$, with a = 14.1361 (5) Å, b = 19.8648 (14) Å, c = 18.2592 (11) Å, β = 96.319 (4)°, and eight formula units per unit cell. Two slightly different molecules exist in the asymmetric unit, and both are characterized by having chelating bidentate nitrate groups at each copper center, a hydroxide bridge, and a nitrate with a single bridging oxygen atom. Copper–copper separations of 3.134 Å are found for both molecules, but the Cu–O(H)–Cu bridge angles are different (114.1, 112.6°). This complex is strongly spin coupled ($-2J$ = 501 cm^{-1}).

Introduction

Spin–spin interactions between paramagnetic metal centers in binuclear complexes are frequently transmitted by a superexchange mechanism via ligand entities that bridge the two metal centers.[2,3] Both single-atom and multiatom bridges are known to propagate exchange with the magnitude of the exchange interaction being dependent upon the bridge identity, its length, the angle subtended at the bridge, the metal–bridge ligand bond lengths, the metal ion stereochemistry, etc. We have examined binuclear copper(II) complexes of a variety of phthalazine and pyridazine ligands (Figure 1) involving nitrogen donors, in which the binuclear centers have multiple bridges leading to superexchange between the copper atoms.[4-17] The diazine, N–N, fragment found in the pyridazine and phthalazine entities, is the common focus of these binucleating ligands and additional bridging groups include hydroxide, in most cases, halides, and bidentate anions, e.g. nitrate, sulfate, and iodate. Ligands of the type PAPR, PTP, and RBITB (Figure 1) generate six-membered chelate rings, and in almost all cases so far studied, triple bridges exist between the two copper atoms (Figure 2a–c). When Y (Y = non-hydroxide bridge) is halide (Cl, Br), copper–copper separations fall in the range 3.00–3.14 Å, but when Y is a triatomic bidentate anion bridge (e.g. NO_3, SO_4, IO_3), larger metal–metal separations result (3.14–3.22 Å) (Figure 2b).[4-6,8,10-13,16] Ligands that generate five-membered chelate rings (PPD, PPDMe, MIP, HPHR) of necessity cause larger metal–metal separations. Copper–copper distances for these complexes are much larger and fall in the range 3.29–3.46 Å, and as a result, bridging ligands, in addition to hydroxide, cannot span the two metal centers. Consequently only dibridged structures are found for systems of this sort (Figure 2d–f).[7,9,14,15,17] The pyrazolylpyridazine ligands (PPD, PPDMe) are similar to the ligand DPPN (3,6-bis(pyrid-2-yl)pyridazine), which has been shown to form analogous complexes.[18-21]

Structurally all of the hydroxo-bridged complexes involve "magnetically symmetric" binuclear centers with distorted, five-coordinate copper ion stereochemistries. In most cases the distortion approximates a square-pyramidal situation with nominally $d_{x^2-y^2}$ ground state copper centers. In these cases each copper atom is bound via an equatorial interaction to both the hydroxide bridge and the diazine bridge. This leads to a situation where magnetic interactions via these groups are the most relevant. Any axial bridge interaction is regarded as "nonmagnetic". In one case, [Cu_2(EtBITP)(OH)Cl_3]·DMF, a trigonal-bipyramidal structure exists in which the hydroxide bridge is bound to the two copper centers via an axial interaction and the diazine bridge is bound equatorially.[16]

Two complexes, [Cu_2(PTP)Cl_4]·CH_3CH_2OH (Figure 2c) and [Cu_2(PAP46Me)Cl_4], have been shown to have triple-bridged structures involving two chlorine bridges, in an asymmetric binuclear center.[13] The essentially square-pyramidal copper centers

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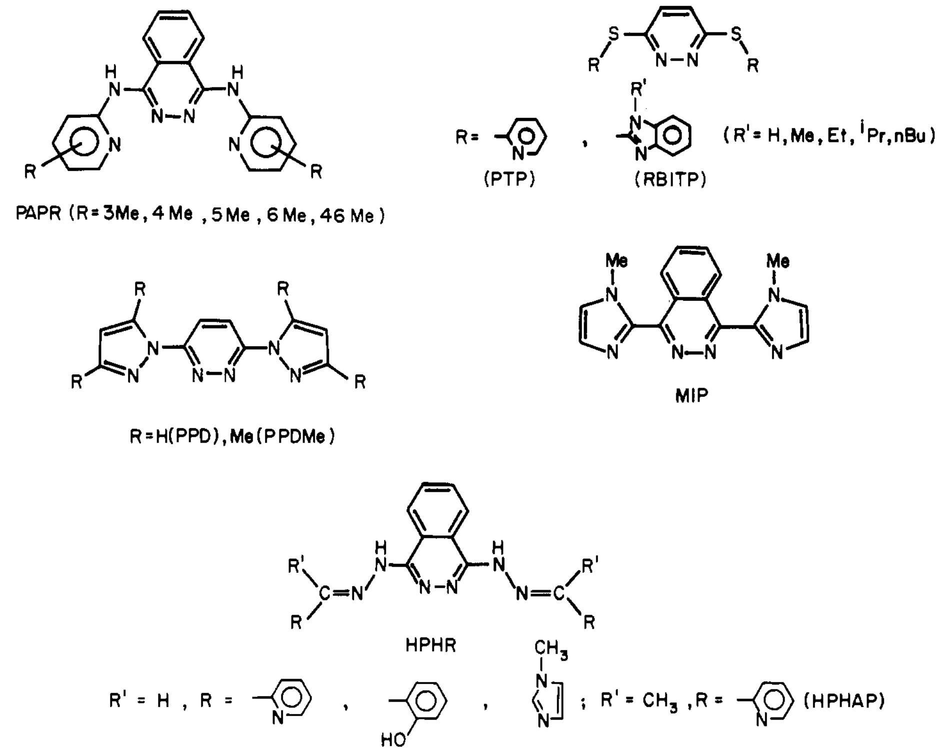

Figure 1. Structures of binucleating phthalazine and pyridazine ligands.

are each bound via an axial and an equatorial interaction to each chlorine bridge, thus creating an effectively "nonmagnetic" superexchange pathway via these bridge groups. An equatorial interaction from each copper atom to the diazine bridge, in each case, generates a viable superexchange pathway.

In the present study we report the full structural details for the complex $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$, which contains two different hydroxide-bridged binuclear molecules in the asymmetric unit, and variable-temperature magnetic studies (5–300 K) on this compound and a number of others, whose structures have already been reported. A very large range of values of the exchange integral ($-2J$ = 55–1304 cm^{-1}) has been observed for the diazine complexes and will be discussed in the light of structural features, bridge groups, chelate ring sizes, and the polarizing nature of the nonbridging ligands.

Experimental Section

Preparation of the Complexes. $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX). This complex was prepared by a modification of the procedure already described.[22] PAP6Me (0.50 g; 1.5 mmol) was added to a hot solution of $Cu(NO_3)_2\cdot 3H_2O$ (1.0 g; 4.1 mmol) in 50/50 CH_3CN/H_2O (150 mL) and the mixture heated until all the ligand dissolved. The resulting green solution was filtered hot and allowed to stand at room temperature until green crystals formed. The product was filtered off, washed with a CH_3CN/ether mixture, and air dried.

The other complexes used in this study, I, XI,[10] VI,[4] XII, XVII,[9] and XVI,[7] were synthesized according to published procedures. Satisfactory elemental analyses were obtained in all cases.

Magnetic Measurements. Variable-temperature magnetic susceptibility data were obtained in the range 5–300 K on an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. Main solenoid fields of 1.5 or 2.0 T and a gradient field of 10 T m^{-1} were employed. Susceptibility data are corrected for diamagnetism (Pascal corrections), temperature-independent paramagnetism, and the presence of monomer impurity. $HgCo(NCS)_4$ was used as a calibration standard.

Table I. Crystal Data

empirical formula	$Cu_2C_{20}H_{19}N_9O_{10}\cdot 0.5H_2O$
fw	671.21
cryst syst	monoclinic
space group	$P2_1/a$
a, Å	14.1361 (5)
b, Å	19.8648 (14)
c, Å	18.2592 (11)
β, deg	96.319 (4)
V, Å^3	5096.23
Z	8
ρ(calcd), g cm^{-3}	1.75
μ, mm^{-1}	1.75
radiation; λ, Å	Mo Kα_1; 0.709 30
temp for data collcn, °C	22
index ranges	
h	+15 to −15
k	+21 to −21
l	+19 ω −19
no. of reflcns measd	6897
no. of unique reflcns	6707
no. of reflcns with $I > 2.5\sigma(I)$	3365
R	0.059
R_w	0.065

Crystallographic Data Collection and Refinement of the Structure. $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX). Crystals of IX are green. The diffraction intensities of an approximately 0.09 × 0.22 × 0.22 mm crystal were collected with graphite-monochromatized Mo Kα radiation by using the ω scan mode to $2\theta_{max}$ = 45° on a Nonius CAD4 diffractometer. Of a total of 6897 measured reflections, 6707 were unique and 3365 were considered significant with $I_{net} > 2.5\sigma(I_{net})$. Lorentz and polarization factors were applied, but no correction was made for absorption. The cell parameters were obtained by the least-squares refinement of the setting angles of 46 reflections with 2θ = 35–45° (λ(Mo Kα_1) = 0.709 30 Å).

The structure was solved by direct methods using MULTAN,[23] and all the atoms were refined anisotropically with block-diagonal least squares. Final values of R = 0.065 and R_w = 0.074 were obtained with unit weights for the significant data. The geometry of one of the nitrate groups was unreasonable, and so this group was deleted and four peaks from the difference map were included, which gave a more reasonable geometry as a nitrate. The positional parameters of this nitrate were fixed and only the isotropic temperature factors were refined. From this approach final values of R = 0.059 and R_w = 0.065 were obtained with unit weights. H atom positions were calculated. Crystal data are given in Table I, and final atomic positional parameters and equivalent isotropic

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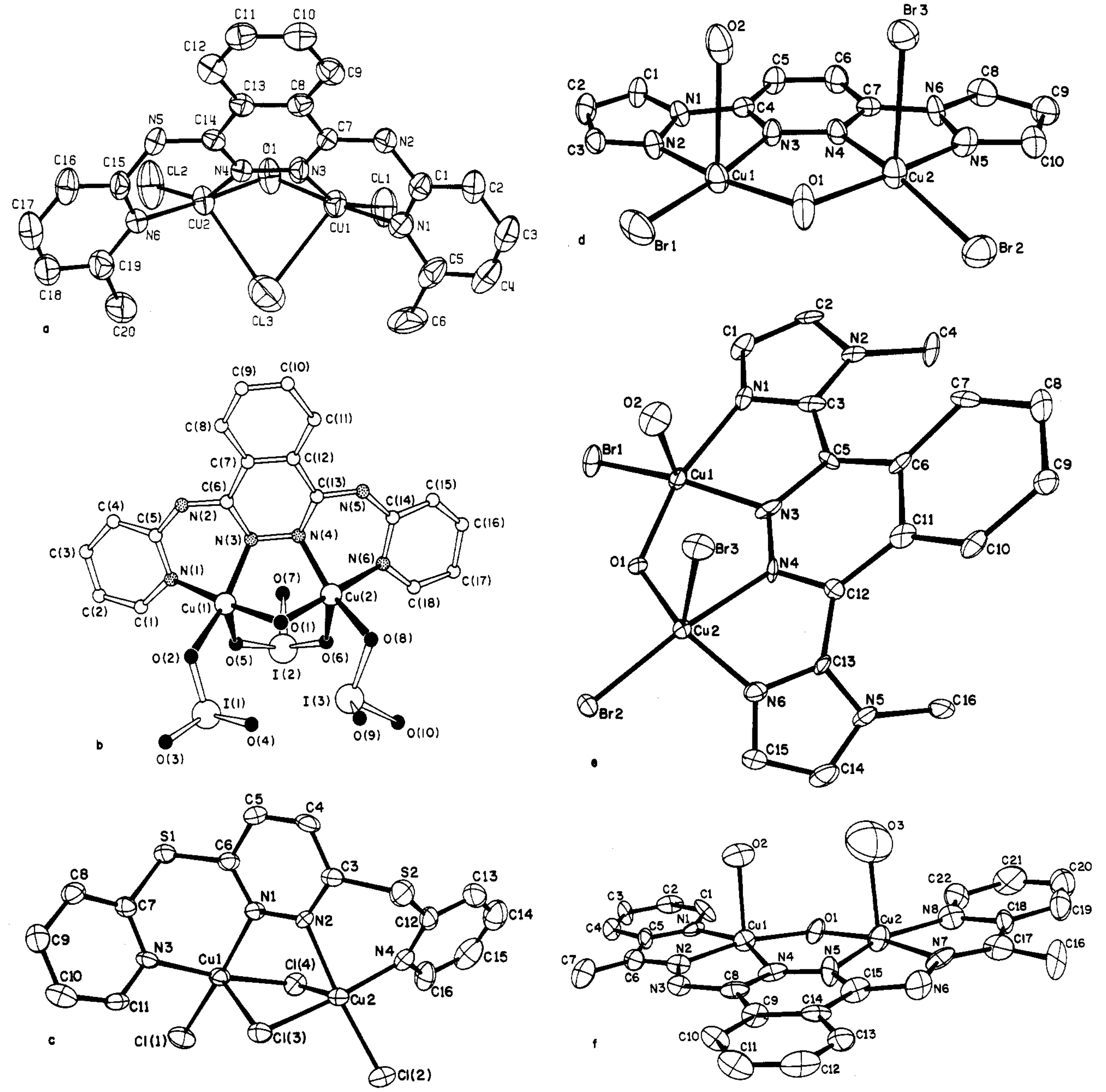

Figure 2. Structural representations of binuclear copper(II) complexes: (a) $[Cu_2(PAP6Me)(OH)Cl_3]\cdot 3H_2O$ (VII); (b) $[Cu_2(PAP)(OH)(IO_3)_3]\cdot 4H_2O$ (VI); (c) $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (II); (d) $[Cu_2(PPD)(OH)Br_3(H_2O)]\cdot 0.6H_2O$ (XVII); (e) $[Cu_2(MIP)(OH)Br_3(H_2O)]\cdot H_2O$ (XVI); (f) $[Cu_2(HPHAP\text{-}H)(OH)(H_2O)_2](ClO_4)_2$ (XV). Distances and angles relevant to the binuclear centers in these compounds are given in Table IV.

temperature factors are given in Table II. All calculations were performed with the NRCVAX system of programs.[24] Scattering factors were taken from ref 25. Anisotropic thermal parameters (Table SI) and a listing of structure factors (Table SII) are included as supplementary material.

Results

Description of the Structure of $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX). The structure of IX is shown in Figure 3. There are two molecules (A and B) in the asymmetric unit of the structure. Interatomic distances and angles relevant to the copper coordination spheres in both molecules and in the coordinated nitrate groups are given in Table III. In each molecular unit the binuclear centers involve two copper(II) ions bridged by the phthalazine diazine group and by a hydroxide oxygen (O(1), O(2)). Copper–oxygen distances to the hydroxide bridges are relatively short (Cu(1)–O(1) = 1.903 (9), Cu(2)–O(1) = 1.864 (9), Cu(3)–O(2) = 1.866 (10), Cu(4)–O(2) = 1.868 (10) Å) with both distances being equal in B. The copper–copper separations are both the same (3.134 (2) Å), but the hydroxide bridge angles are significantly different (Cu(1)–O(1)–Cu(2) = 112.6 (5)°, Cu(3)–O(2)–Cu(4) = 114.1 (5)°). The role of the nitrate groups is very interesting, and in both molecules each copper atom is bound to a chelating, bidentate nitrate. These bidentate nitrates are characterized by having one short Cu–O separation close to 2 Å with a second, much longer contact (2.55–2.67 Å) (Table III). It has been suggested that in unsymmetrically coordinated, bidentate nitrate groups the difference between the Cu–O bond lengths falls in the range 0.2–0.7 Å,[26] which supports the bidentate chelating nature of the nitrate groups in IX. The O–Cu–O angle generated at each copper center by such a nitrate group is, of necessity, small and falls in the range 51–56° (Table III). The third bridging, monodentate nitrate group in each molecule is

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Table II. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX)

atom	*x*	*y*	*z*	B_{iso}, Å^2
Cu(1)	0.20079 (12)	0.35468 (8)	0.74774 (9)	3.23 (7)
Cu(2)	0.08850 (13)	0.35547 (9)	0.88646 (10)	3.86 (8)
Cu(3)	0.17851 (13)	0.13215 (8)	0.22125 (10)	3.89 (8)
Cu(4)	0.05305 (14)	0.12390 (9)	0.35222 (10)	4.22 (9)
O(1)	0.1993 (7)	0.3818 (5)	0.8475 (5)	4.3 (5)
O(2)	0.0722 (8)	0.0945 (5)	0.2578 (6)	5.5 (6)
O(11)	0.2875 (7)	0.4322 (4)	0.7307 (5)	4.2 (5)
O(12)	0.3825 (7)	0.3480 (5)	0.7510 (6)	5.0 (5)
O(13)	0.4359 (7)	0.4458 (5)	0.7213 (7)	5.5 (6)
O(21)	0.1286 (8)	0.4144 (5)	0.9766 (5)	4.8 (5)
O(22)	0.1631 (9)	0.3148 (5)	1.0163 (6)	6.3 (7)
O(23)	0.2173 (8)	0.3998 (6)	1.0792 (6)	6.0 (6)
O(31)	0.8867 (8)	0.3779 (5)	0.7362 (7)	6.9 (7)
O(32)	0.9712 (9)	0.3273 (9)	0.6707 (8)	11.1 (10)
O(33)	1.0352 (7)	0.3985 (4)	0.7490 (6)	4.3 (5)
O(41)	0.1598 (9)	0.0629 (5)	0.1390 (6)	5.8 (6)
O(42)	0.0853 (12)	0.1456 (8)	0.0868 (8)	10.1 (9)
O(43)	0.0728 (16)	0.0478 (10)	0.0402 (8)	14.5 (14)
O(51)	−0.0472 (8)	0.0567 (5)	0.3641 (6)	5.1 (6)
O(52)	−0.1246 (8)	0.1500 (6)	0.3456 (7)	6.8 (6)
O(53)	−0.1984 (8)	0.0610 (7)	0.3739 (7)	7.4 (7)
N(1)	0.1479 (8)	0.2670 (5)	0.7772 (6)	2.9 (5)
N(2)	0.0862 (7)	0.2689 (5)	0.8303 (6)	2.6 (5)
N(3)	0.2027 (7)	0.3208 (5)	0.6456 (6)	2.9 (5)
N(4)	−0.0393 (8)	0.3356 (5)	0.9116 (6)	3.2 (5)
N(5)	0.2357 (7)	0.2101 (5)	0.6965 (6)	2.9 (5)
N(6)	−0.0107 (8)	0.2165 (6)	0.9065 (6)	3.7 (6)
N(7)	0.1533 (8)	0.2189 (5)	0.2719 (6)	3.3 (5)
N(8)	0.1020 (8)	0.2142 (5)	0.3298 (6)	3.0 (5)
N(9)	0.2305 (8)	0.2809 (6)	0.1881 (6)	3.9 (6)
N(10)	0.0214 (8)	0.2625 (5)	0.4227 (6)	3.7 (6)
N(11)	0.2938 (8)	0.1700 (6)	0.1872 (6)	3.8 (5)
N(12)	0.0604 (8)	0.1491 (6)	0.4568 (6)	3.3 (5)
N(1A)	0.3716 (8)	0.4078 (5)	0.7349 (6)	3.6 (5)
N(2A)	0.1693 (8)	0.3753 (6)	1.0257 (6)	3.9 (5)
N(3A)	0.9652 (8)	0.3687 (6)	0.7176 (6)	4.2 (6)
N(4B)	0.1051 (12)	0.0858 (8)	0.0885 (7)	7.5 (9)
N(5B)	−0.1272 (9)	0.0892 (7)	0.3596 (7)	5.3 (7)
C(1)	0.1584 (10)	0.0272 (7)	0.7909 (9)	3.9 (7)
C(2)	0.1034 (11)	0.0283 (7)	0.8499 (8)	4.3 (8)
C(3)	0.1812 (9)	0.0841 (6)	0.7579 (8)	3.1 (6)
C(4)	0.0681 (11)	0.0892 (7)	0.8716 (8)	4.3 (7)
C(5)	0.1510 (9)	0.1462 (6)	0.7823 (7)	2.8 (6)
C(6)	0.0919 (8)	0.1487 (6)	0.8383 (7)	2.7 (6)
C(7)	0.1770 (8)	0.2099 (6)	0.7514 (7)	2.4 (5)
C(8)	0.0563 (9)	0.2139 (6)	0.8575 (7)	2.9 (6)
C(9)	0.2349 (9)	0.2564 (6)	0.6389 (7)	3.0 (6)
C(10)	0.2668 (10)	0.2351 (7)	0.5720 (8)	3.7 (7)
C(11)	0.2651 (10)	0.2774 (7)	0.5145 (7)	3.8 (7)
C(12)	0.2247 (10)	0.3405 (8)	0.5204 (8)	4.0 (7)
C(13)	0.1941 (10)	0.3629 (7)	0.5856 (7)	3.7 (6)
C(14)	0.1484 (12)	0.4313 (8)	0.5932 (10)	5.5 (9)
C(15)	−0.0697 (9)	0.2724 (7)	0.9213 (7)	3.4 (7)
C(16)	−0.1527 (10)	0.2573 (8)	0.9467 (8)	4.0 (7)
C(17)	−0.2129 (11)	0.3104 (8)	0.9639 (9)	4.9 (8)
C(18)	−0.1833 (10)	0.3741 (8)	0.9513 (8)	4.3 (7)
C(19)	−0.0987 (11)	0.3868 (8)	0.9247 (7)	4.0 (7)
C(20)	−0.0654 (11)	0.4572 (7)	0.9070 (9)	4.6 (8)
C(21)	0.1205 (11)	0.4602 (6)	0.2759 (8)	3.9 (7)
C(22)	0.0727 (11)	0.4554 (6)	0.3365 (9)	4.6 (8)
C(23)	0.1532 (11)	0.4036 (7)	0.2437 (8)	4.0 (7)
C(24)	0.0529 (11)	0.3931 (7)	0.3668 (8)	4.4 (7)
C(25)	0.1375 (10)	0.3399 (6)	0.2740 (7)	3.1 (6)
C(26)	0.0863 (10)	0.3343 (6)	0.3331 (8)	3.4 (6)
C(27)	0.1731 (10)	0.2781 (6)	0.2445 (7)	3.2 (6)
C(28)	0.0708 (9)	0.2674 (6)	0.3614 (7)	2.8 (6)
C(29)	0.2993 (10)	0.2370 (7)	0.1722 (7)	3.4 (7)
C(30)	0.3769 (12)	0.2637 (8)	0.1420 (8)	4.7 (8)
C(31)	0.4498 (12)	0.2218 (9)	0.1262 (9)	5.7 (9)
C(32)	0.4412 (11)	0.1526 (9)	0.1415 (9)	5.3 (8)
C(33)	0.3661 (10)	0.1279 (8)	0.1734 (8)	4.7 (8)
C(34)	0.3607 (12)	0.0530 (7)	0.1928 (10)	5.5 (9)
C(35)	0.0296 (10)	0.2105 (7)	0.4747 (7)	3.5 (6)
C(36)	0.0032 (10)	0.2230 (7)	0.5442 (8)	4.1 (7)
C(37)	0.0126 (11)	0.1724 (8)	0.5957 (8)	4.4 (7)
C(38)	0.0509 (10)	0.1113 (8)	0.5784 (8)	4.5 (7)
C(39)	0.0768 (10)	0.1000 (7)	0.5078 (7)	3.6 (7)
C(40)	0.1216 (13)	0.0343 (8)	0.4855 (10)	5.6 (9)
O(3)	0.3695 (13)	0.4097 (9)	0.9539 (10)	12.4 (5)
N(6B)	0.3196 (0)	0.1316 (0)	0.3903 (0)	8.7 (5)
O(61)	0.2515 (0)	0.0960 (0)	0.3472 (0)	8.1 (3)
O(62)	0.3523 (0)	0.1250 (0)	0.4453 (0)	10.1 (4)
O(63)	0.3451 (0)	0.1776 (0)	0.3585 (0)	12.1 (5)
H(1)	0.182	−0.021	0.771	4.7
H(2)	0.086	−0.018	0.878	5.1
H(3)	0.224	0.083	0.711	3.8
H(4)	0.023	0.090	0.917	5.2
H(10)	0.292	0.183	0.566	4.5
H(11)	0.295	0.262	0.464	4.5
H(12)	0.218	0.375	0.472	4.9
H(16)	−0.174	0.204	0.954	4.8
H(17)	−0.281	0.301	0.986	5.5
H(18)	−0.229	0.417	0.963	5.2
H(21)	0.131	0.510	0.252	4.4
H(22)	0.050	0.502	0.363	5.2
H(23)	0.193	0.408	0.196	5.1
H(24)	0.013	0.389	0.416	5.5
H(30)	0.381	0.317	0.130	5.5
H(31)	0.513	0.241	0.102	6.5
H(32)	0.497	0.118	0.127	5.8
H(36)	−0.026	0.273	0.557	5.2
H(37)	−0.009	0.181	0.651	5.0
H(38)	0.061	0.071	0.620	5.2

bound in a most unusual manner with one oxygen atom occupying an apical, bridging position between the two copper centers with very long copper–oxygen contacts, one of which is substantially shorter than the other. (Cu(1)–O(33) = 2.500 (10), Cu(2)–O(33) = 2.680 (10), Cu(3)–O(61) = 2.870 (2), Cu(4)–O(61) = 2.519 (2) Å). These copper–oxygen bond distances are much longer than those observed for a copper nitrate complex of 2,2′-bipyrimidine, which has two monodentate nitrate bridge groups (Cu–O = 1.965, 2.300 Å).[27] The Cu–O(NO$_3$)–Cu bridge angles (Cu(1)–O(33)–Cu(2) = 74.4 (3), Cu(3)–O(61)–Cu(4) = 70.78 (6)°) are much smaller than those generated by the hydroxide bridge, and the bridging nitrate is bent toward the phthalazine group (Cu(1)–O(33)–N(3A) = 122.1 (8), Cu(2)–O(33)–N(3A) = 114.2 (8), Cu(3)–O(61)–N(6B) = 124.58 (4), Cu(4)–O(61)–N(6B) = 120.63 (4)°).

The copper ion stereochemistries are distorted tetragonal with four short in-plane contacts involving a hydroxide bridge, phthalazine and pyridine nitrogens, and one oxygen atom from a bidentate nitrate. The long axial contacts involve the other oxygen atom of the bidentate nitrates and the single-atom-bridging nitrate group. The copper centers are displaced from the mean planes of the four equatorial N_2O_2 donors (Cu(1), 0.142 (5) Å; Cu(2), 0.141 (6) Å; Cu(3), 0.190 (6) Å; Cu(4), 0.133 (6) Å), and other, fairly severe, distortions exist within each copper ion coordination sphere (Table III), which can be associated with the geometrical constraints imposed by the chelating, bidentate nitrate groups. In each molecule the ligand adopts a twisted conformation where the phthalazine and pyridine rings resemble the body and claws of a lobster. In molecule A the pyridine rings (1, 3) are twisted by 26.9 (4) and 28.9 (4)°, respectively, with respect to the phthalazine mean plane (2) and are mutually inclined by 53.4 (5)°. In molecule B the pyridine rings (4, 6) are twisted by 25.2 (4) and 30.4 (4)°, respectively, and are mutually inclined by 49.9 (5)° (data on least-squares planes are given in Table SIV, supplementary material).

The structure of IX can be compared with that of a related compound $[Cu_2(PAP46Me)(OH)(NO_3)_2(H_2O)]NO_3$ (XI),[10] involving the ligand 1,4-bis((4,6-dimethylpyrid-2-yl)amino)phthalazine. In this complex a five-coordinate, square-pyramidal

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[27] De Munno, G.; Bruno, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 2030.

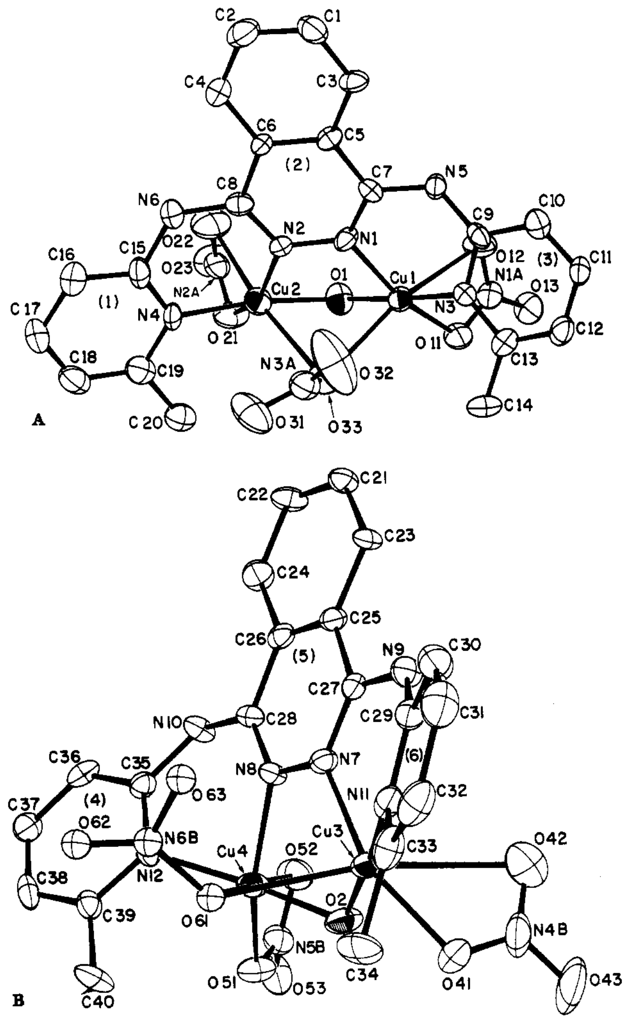

Figure 3. Structural representation of $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX) with hydrogen atoms omitted (40% probability thermal ellipsoids), showing both molecules (A and B) in the asymmetric unit.

copper(II) center and a tetragonally distorted six-coordinate copper(II) center are bridged by the phthalazine group and a hydroxide only, with one chelating, bidentate nitrate bound to each copper center and the third nitrate behaving as an ion. Comparable copper–oxygen separations to both nitrate groups and the hydroxide bridge are found in both systems, although the long copper–oxygen (nitrate) contacts in IX are somewhat longer than those in XI. The average copper–copper separation and hydroxide bridge angle in IX are slightly less than those in XI. The complex $[Cu_2(PAP4Me)(OH)(H_2O)_2(NO_3)_2]NO_3$ (VIII), involving the ligand 1,4-bis((4-methylpyrid-2-yl)amino)phthalazine, has a rather different structure with the common phthalazine and hydroxide bridge, but in addition a bidentate nitrate group also bridges the two copper centers.[8] Six-coordination is completed by a chelating bidentate nitrate at one copper center and two water molecules at the other. The binuclear center dimensions do not differ appreciably within this group of nitrate derivatives (VIII, IX, XI), but the largest copper–copper separation (3.156 (2) Å), which is found for XI, may just be too large to accommodate either a monodentate or bidentate bridging nitrate group. The double-bridged nitrate complex $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2]NO_3\cdot H_2O$ (XII), which involves five-membered chelate rings, has a much larger copper–copper separation than IX and XI (3.338 Å),[9] thus effectively preventing the formation of a third bridge group between the metal centers. In this system one nitrate is considered to be a bidentate ligand to one metal center while the other coordinated nitrate acts in a monodentate fashion bound to the other metal.

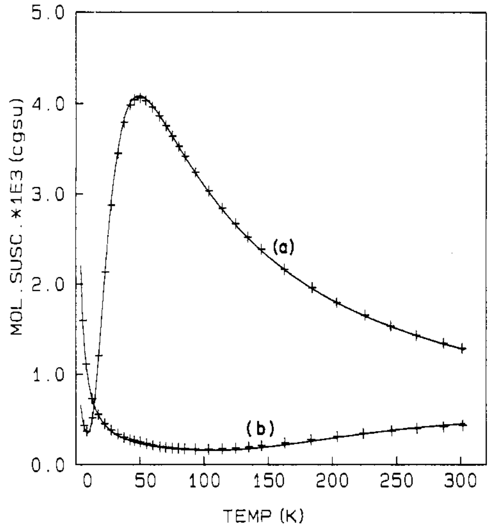

Figure 4. Magnetic susceptibility data for $[Cu_2(PAP46Me)Cl_4]$ (I) (a) and $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX) (b). The solid lines were calculated from (1) with $g = 2.05 \pm 0.002$, $-2J = 55.2 \pm 0.09$ cm^{-1}, and $\rho = 0.006$ for curve a and $g = 2.04 \pm 0.006$, $-2J = 501 \pm 4$ cm^{-1}, and $\rho = 0.022$ for curve b.

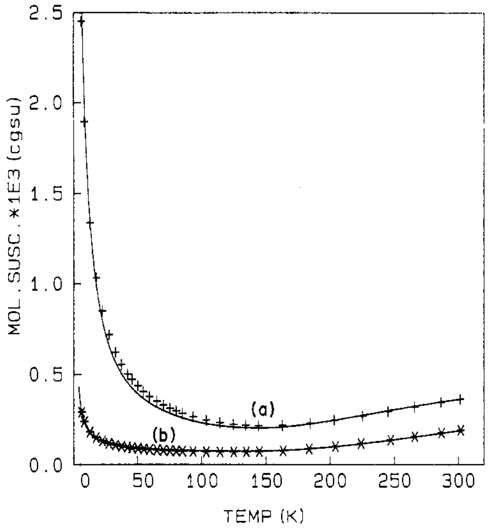

Figure 5. Magnetic susceptibility data for $[Cu_2(PAP46Me)(OH)(NO_3)_2(H_2O)]\cdot NO_3$ (XI) (a) and $[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2]\cdot NO_3\cdot H_2O$ (XII) (b). The solid lines were calculated from (1) with $g = 2.05 \pm 0.02$, $-2J = 597 \pm 0.5$ cm^{-1}, and $\rho = 0.042$ for curve a and $g = 2.07 \pm 0.009$, $-2J = 770 \pm 3$ cm^{-1}, and $\rho = 0.0037$ for curve b.

Magnetic Measurements. Magnetic susceptibility measurements were performed on powdered samples of I, VI (repeat of earlier work), IX, XI, XII (repeat of earlier work), XVI, and XVII in the temperature range 5–300 K, and the results are summarized in Table IV and Figures 4–6. The best fit lines, in each case, were calculated from the modified Van Vleck equation[28] for exchange-coupled pairs of copper(II) ions (eq 1). In this expression $2J$ (in the spin Hamiltonian $H = -2J\hat{S}_1\cdot\hat{S}_2$) is the singlet–triplet splitting or exchange integral and other symbols have their usual meaning. ρ represents the fraction of a possible magnetically dilute copper(II) impurity. The temperature independent paramagnetism for a binuclear copper(II) complex, $N\alpha$, was taken as 120×10^{-6} cgsu/mol unless otherwise stated.

$$\chi_m = \frac{N\beta^2g^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-\rho) + \left[\frac{N\beta^2g^2}{4kT}\right]\rho + N\alpha \qquad (1)$$

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(28) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*, Oxford University Press: London, 1932; Chapter 9.

Table III. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX)

Cu(1)–Cu(2)	3.1339 (23)	Cu(3)–Cu(4)	3.1344 (25)
Cu(1)–O(1)	1.903 (9)	Cu(3)–O(2)	1.866 (10)
Cu(1)–O(11)	2.013 (9)	Cu(3)–O(41)	2.032 (10)
Cu(1)–O(12)	2.566 (10)	Cu(3)–O(42)	2.668 (14)
Cu(1)–O(33)	2.500 (10)	Cu(3)–N(7)	2.006 (10)
Cu(1)–N(1)	1.993 (10)	Cu(3)–N(11)	1.956 (12)
Cu(1)–N(3)	1.986 (10)	Cu(3)–O(61)	2.5192 (19)
Cu(2)–O(1)	1.864 (9)	Cu(4)–O(2)	1.868 (10)
Cu(2)–O(21)	2.049 (10)	Cu(4)–O(51)	1.976 (10)
Cu(2)–O(22)	2.615 (12)	Cu(4)–O(52)	2.554 (12)
Cu(2)–O(33)	2.680 (10)	Cu(4)–N(8)	1.982 (10)
Cu(2)–N(2)	2.000 (10)	Cu(4)–N(12)	1.966 (10)
Cu(2)–N(4)	1.952 (10)	Cu(4)–O(61)	2.8703 (20)
O(1)–Cu(1)–O(11)	90.2 (4)	O(33)–Cu(1)–N(1)	85.5 (4)
O(1)–Cu(1)–O(12)	96.3 (4)	O(33)–Cu(1)–N(3)	103.7 (4)
O(1)–Cu(1)–O(33)	77.5 (4)	N(1)–Cu(1)–N(3)	90.1 (4)
O(1)–Cu(1)–N(1)	86.8 (4)	O(1)–Cu(2)–O(33)	73.4 (4)
O(1)–Cu(1)–N(3)	176.6 (4)	O(1)–Cu(2)–N(2)	90.7 (4)
O(11)–Cu(1)–O(12)	54.4 (3)	O(1)–Cu(2)–N(4)	169.7 (5)
O(11)–Cu(1)–O(33)	108.8 (3)	O(21)–Cu(2)–O(22)	53.1 (4)
O(11)–Cu(1)–N(1)	164.4 (4)	O(21)–Cu(2)–O(33)	126.5 (3)
O(11)–Cu(1)–N(3)	92.5 (4)	O(21)–Cu(2)–N(2)	153.0 (4)
O(12)–Cu(1)–O(33)	162.5 (3)	O(21)–Cu(2)–N(4)	96.2 (4)
O(12)–Cu(1)–N(1)	110.7 (4)	O(22)–Cu(2)–O(33)	172.6 (3)
O(12)–Cu(1)–N(3)	83.5 (4)	O(22)–Cu(2)–N(2)	100.4 (4)
O(22)–Cu(2)–N(4)	90.9 (4)	O(2)–Cu(4)–O(51)	94.0 (4)
O(33)–Cu(2)–N(2)	78.9 (3)	O(2)–Cu(4)–O(52)	105.2 (5)
O(33)–Cu(2)–N(4)	96.5 (4)	O(2)–Cu(4)–N(8)	90.2 (4)
N(2)–Cu(2)–N(4)	89.0 (4)	O(2)–Cu(4)–N(12)	168.1 (5)
O(1)–Cu(2)–O(21)	88.6 (4)	O(2)–Cu(4)–O(61)	70.6 (4)
O(1)–Cu(2)–O(22)	99.2 (4)	O(51)–Cu(4)–O(52)	55.2 (4)
O(2)–Cu(3)–O(41)	87.1 (4)	O(51)–Cu(4)–N(8)	154.8 (4)
O(2)–Cu(3)–O(42)	91.9 (5)	O(51)–Cu(4)–N(12)	91.6 (4)
O(2)–Cu(3)–N(7)	89.3 (4)	O(51)–Cu(4)–O(61)	126.0 (3)
O(2)–Cu(3)–N(11)	177.2 (5)	O(52)–Cu(4)–N(8)	99.8 (4)
O(2)–Cu(3)–O(61)	79.9 (4)	O(52)–Cu(4)–N(12)	86.6 (4)
O(41)–Cu(3)–O(42)	51.5 (5)	O(52)–Cu(4)–O(61)	175.5 (3)
O(41)–Cu(3)–N(7)	155.1 (5)	N(8)–Cu(4)–N(12)	89.3 (4)
O(41)–Cu(3)–N(11)	94.0 (5)	N(8)–Cu(4)–O(61)	78.7 (3)
O(41)–Cu(3)–O(61)	119.2 (3)	N(12)–Cu(4)–O(61)	97.6 (3)
O(42)–Cu(3)–N(7)	104.1 (5)	Cu(1)–O(1)–Cu(2)	112.6 (5)
O(42)–Cu(3)–N(11)	90.8 (5)	Cu(3)–O(2)–Cu(4)	114.1 (5)
O(42)–Cu(3)–O(61)	168.3 (3)	Cu(1)–O(33)–N(3A)	122.1 (8)
N(7)–Cu(3)–N(11)	90.7 (4)	Cu(2)–O(33)–N(3A)	114.2 (8)
N(7)–Cu(3)–O(61)	84.3 (3)	Cu(3)–O(61)–N(6B)	124.58 (4)
N(11)–Cu(3)–O(61)	97.4 (3)	Cu(4)–O(61)–N(6B)	120.63 (4)

The parameters giving the best fit were obtained by using nonlinear regression analyses with ρ, g, and $2J$ as floating parameters.

Discussion

A remarkable variation in spin exchange between the copper(II) centers is observed for the binuclear diazine complexes I–XVII (Table IV). $-2J$ values span a low value for the complex $[Cu_2(PAP46Me)Cl_4]$ (I) of 55 cm^{-1} to a high value of 1304 cm^{-1} for the complex $[Cu_2(PPD)(OH)Br_3]\cdot 0.6H_2O$ (XVII). A graphical representation of exchange ($-2J$), as a function of Cu–O(H)–Cu bridge angle, for the hydroxo-bridged complexes is shown in Figure 7. The hydroxo-bridged compounds can be divided roughly into two groups; those involving six-membered chelate rings and those involving five-membered chelate rings (see Figure 2 for examples). As a result of the geometrical consequences imposed by these chelate rings, Cu–O(H)–Cu bridge angles fall into two ranges: 100–116 and 116–127°, respectively. Copper–copper separations lie between 2.99 and 3.22 Å for the six-membered chelate ring systems and between 3.29 and 3.46 Å for the five-membered chelate ring systems, and within the former group, which for the most part has triply bridged binuclear centers, the metal–metal separation is influenced, in large measure, by the dimensions of the bridge group, Y (Table IV). The ability to "tune" the binuclear center dimensions has led to a situation where for species with the same copper ion ground state ($d_{x^2-y^2}$) a linear relationship is found between $-2J$ and the hydroxide bridge angle for a number of systems.[7,8,10] The straight line depicted in Figure 7 represents the linear regression analysis (eq 2) of the exchange versus hydroxide bridge angle data for compounds III, IV, and VII–X.

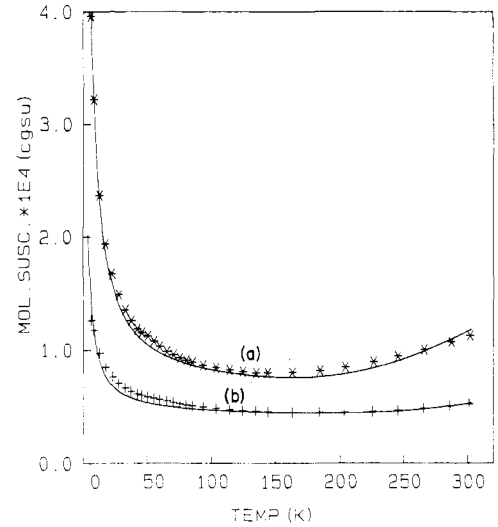

Figure 6. Magnetic susceptibility data for $[Cu_2(MIP)(OH)Br_3(H_2O)]\cdot H_2O$ (XVI) (a) and $[Cu_2(PPD)(OH)Br_3(H_2O)]\cdot 0.6H_2O$ (XVII). (b) The solid lines were calculated from (1) with $g = 2.17 \pm 0.01$, $-2J = 992 \pm 16$ cm^{-1}, and $\rho = 0.005$ for curve a and $g = 2.08 \pm 0.03$, $-2J = 1304 \pm 72$ cm^{-1}, and $\rho = 0.0016$ ($N\alpha = 40 \times 10^{-6}$ cgsu) for curve b.

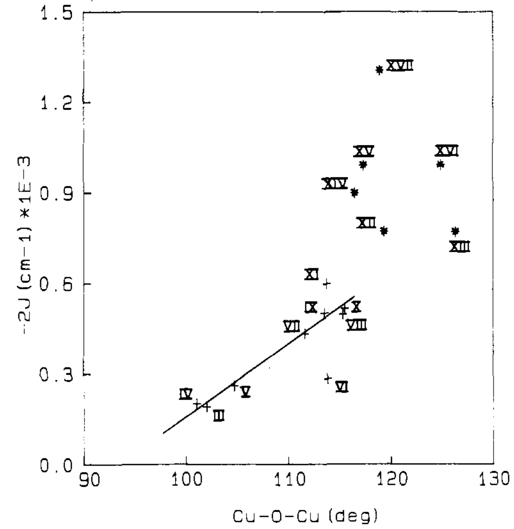

Figure 7. Graphical representation of exchange integral ($-2J$) as a function of Cu–O(H)–Cu bridge angle for hydroxo-bridged diazine complexes. A plus sign indicates compounds with 6-membered chelate rings; an asterisk indicates compounds with 5-membered chelate rings. The straight line depicts the linear regression analysis of the $-2J$ vs Cu–O–Cu data for compounds III, IV, and VII–X ($-2J = 23.06\alpha - 2143$ cm^{-1}).

$$-2J = 23.06\alpha - 2143 \text{ cm}^{-1} \qquad (2)$$

Although compound XIII was included in an earlier analysis,[7,10] it has been excluded here, along with XI, because these compounds have double-bridged, as opposed to triple-bridged binuclear centers. Compound IX is included in the analysis for the first time. The linear dependence of the single–triplet splitting on hydroxide bridge angle for binuclear copper(II) complexes has been well documented for a series of dihydroxo-bridged copper(II) complexes of the sort $[CuL(OH)_2LCu]^{2+}$ (L = bidentate N_2 donor).[29] Antiferromagnetic coupling was observed for angles above 97.5° with ferromagnetic coupling at smaller angles. In the present study

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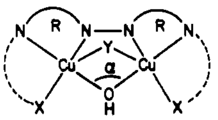
[29] Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

Table IV. Magnetic and Structural Data



compd	Cu–O(H)–Cu (α), deg	Cu–O(H)(av), Å	Cu–Cu, Å	X	Y	$-2J$, cm^{-1}	R	$-2J/\alpha$ (ϕ)	ref
$[Cu_2(PAP46Me)Cl_4$ (I)			3.251	Cl	Cl	55	6		
$[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (II)			3.198	Cl	Cl	131	6		24
$[Cu_2(PAP)(OH)Br_3]\cdot 1.5H_2O$ (III)	102.9	1.93	3.010	Br	Br	190	6	1.86	4
	101.3	1.93	2.984						
$[Cu_2(PAP)(OH)Cl_3]\cdot 1.5H_2O$ (IV)	101.8	1.93	3.001	Cl	Cl	200	6	1.98	4
	100.1	1.94	2.972						
$[Cu_2(EtBITP)(OH)Cl_3]\cdot DMF$ (V)	104.7	1.91	3.017	Cl	Cl	260	6	2.48	16
$[Cu_2(PAP)(OH)(IO_3)_3]\cdot 4H_2O$ (VI)	113.8	1.89	3.165	IO_3	IO_3	283	6	2.48	
$[Cu_2(PAP6Me)(OH)Cl_3]\cdot 3H_2O$ (VII)	111.6	1.90	3.138	Cl	Cl	432	6	3.87	10
$[Cu_2(PAP4Me)(OH)(H_2O)_2(NO_3)_2]NO_3$ (VIII)	115.3	1.86	3.138	H_2O NO_3	NO_3	497	6	4.31	8
$[Cu_2(PAP6Me)(OH)(NO_3)_3]\cdot 0.5H_2O$ (IX)	114.4	1.87	3.134	NO_3	NO_3	501	6	4.42	
	112.6	1.88							
$[Cu_2(PAP)(OH)Cl(SO_4)]\cdot 2H_2O$ (X)	115.5	1.90	3.211	Cl H_2O	SO_4	516	6	4.47	8
$[Cu_2(PAP46Me)(OH)(NO_3)_2(H_2O)]NO_3$ (XI)	113.7	1.89	3.156	NO_3		597	6	5.25	
$[Cu_2(PPDMe)(OH)(NO_3)_2(H_2O)_2]NO_3\cdot H_2O$ (XII)	119.3	1.93	3.338	H_2O NO_3		770	5	6.45	
$[Cu_2(MIP)(OH)Cl_3(H_2O)]\cdot H_2O$ (XIII)	126.3	1.92	3.425	Cl		770	5	6.10	7
$[Cu_2(PPD)(OH)Cl_3(H_2O)]\cdot 0.8H_2O$ (XIV)	116.4	2.03	3.454	Cl		898	5	7.73	17
$[Cu_2(HPHAP\text{-}H)(OH)(H_2O)_2](ClO_4)_2\cdot H_2O$ (XV)	117.3	1.93	3.295	pyridine		990	5	8.44	15
$[Cu_2(MIP)(OH)Br_3(H_2O)]\cdot H_2O$ (XVI)	124.9	1.93	3.420	Br		992	5	7.94	
$[Cu_2(PPD)(OH)Br_3(H_2O)]\cdot 0.6H_2O$ (XVII)	118.9	1.98	3.413	Br		1304	5	11.1	

extrapolation of the straight line plot (Figure 7) would give $J = J_F + J_{AF} = 0$ at a smaller hydroxide bridge angle of 92.9°.

The dichloro-bridged complexes I and II have structurally similar asymmetric, binuclear centers (see Figure 2c for structure of II) in which each square-pyramidal copper(II) ion is bridged by an equatorial and an axial interaction to each chlorine bridge.[13] Although chlorine bridges are known to be superexchange active, the orientation of the magnetic metal orbitals in these complexes is such that effectively no antiferromagnetic exchange would be expected to occur via these bridge groups. A similar situation has been observed for a number of oxalate-bridged binuclear copper complexes.[30] Since the exchange for II ($-2J = 131$ cm^{-1}) is substantially larger than that observed for I ($-2J = 55$ cm^{-1}), it is reasonable to assume that the pyridazine bridge is a better superexchange medium than phthalazine. This observation is also supported by the fact that for the pyridazine complexes XIV and XVII much larger values of $-2J$ are observed than for the corresponding phthalazine complexes XIII and XVI, all of which have similar square-pyramidal structures, even though the hydroxide bridge angles are smaller for the PPD complexes. In addition complex V, $[Cu_2(EtBITP)(OH)Cl_3]\cdot DMF$,[16] which has a trigonal-bipyramidal structure, falls on the straight line describing compounds III, IV, and VII–X (Figure 7). This is purely fortuitous but indicates that if this complex had involved square-pyramidal copper(II) centers, the exchange would have been larger, thus indicating again that pyridazine is a better superexchange bridge than phthalazine.

The superexchange observed for all the complexes under discussion is mediated by more than one bridge group, and since in all cases involving triple bridges the bridge group Y (Table IV) occupies a coordination site axial to both square-pyramidal copper centers, then antiferromagnetic spin exchange via such a group is effectively zero. Therefore the hydroxide and diazine bridges control the exchange process, and for most complexes the hydroxide bridge is considered to be the dominant exchange pathway. Examples of binuclear copper(II) complexes involving just diazine bridges are rare, but in a series of dibridged copper(II) complexes of the ligand μ-3,5-bis(pyridin-2-yl)-1,2,4-triazole, involving two in-plane diazine groups bridging two six-coordinate copper centers, exchange integrals ($-2J$) were observed in the range 204–236 cm^{-1}.[31] Also the complex $[Cu_2(PTP)_2Cl](ClO_4)_3\cdot CH_3CN$, which involves a tribridged structure with two pyridazine groups bridging the two square-pyramidal copper centers via equatorial interactions and an axially bound bridging chlorine, is antiferromagnetically coupled with $-2J = 480$ cm^{-1}.[32] This exchange situation can be attributed to the pyridazine bridge groups, since the apical chlorine bridge would not be a magnetic bridge group, and indicates quite a strong exchange for pyridazine.

Quantifying the individual contributions to the total superexchange picture in these multibridged systems is speculative based on these limited data. However the straight-line relationship indicated in Figure 7 is predicated on the reasonable assumption that the phthalazine entity provides a roughly constant contribution to the total exchange. Two phthalazine complexes (VI, XI) emerge as anomalous with respect to the straight-line exchange relationship. Compound VI, $[Cu_2(PAP)(OH)(IO_3)_3]\cdot 4H_2O$, involves a binuclear center bridged by hydroxide and bidentate iodate, in addition to the diazine bridge, and exhibits a pronounced trigonal-bipyramidal distortion.[6] Assuming a d_{z^2} ground state, the hydroxide bridge is bound via an axial interaction, while the diazine nitrogens are bound equatorially. In such a situation it would be reasonable to expect a reduced exchange. Complex XI, $[Cu_2(PAP46Me)(OH)(NO_3)_2(H_2O)]NO_3$, has a somewhat larger exchange than would be expected, based on the general structural similarity between this compound and IX, and it is not immediately obvious why this should be so.

The effect of changing the chelate ring size (R) from six to five for the phthalazine systems results in a dramatic change in the dimensions of the binuclear center, with a marked increase in the copper–copper separation and hydroxide bridge angle, leading to much stronger exchange. The phthalazine complexes XIII, XV, and XVI, which involve five-membered chelate rings, have values of $-2J$ of 770 cm^{-1} or greater. However, a comparison of these three compounds suggests that, despite the general similarities of the binuclear centers (Figure 2), other factors besides the hydroxide and phthalazine bridge are influencing the exchange situation. On the reasonable assumption that the essentially planar binuclear centers for these three compounds, which involve in-plane

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magnetic interactions between the metal $d_{x^2-y^2}$ orbitals and the hydroxide and phthalazine bridges, would be expected to exhibit spin exchange based predominantly on the hydroxide bridge itself and that the hydroxide bridge angle would be a dominant influence, then the parameter ϕ (Table IV) ($\phi = -2J/(\text{Cu-O(H)-Cu})$ = 6.10, 7.94, and 8.44 for XIII, XV, and XVI, respectively) indicates that factors other than the bridge angle are contributing to the total exchange.

Displacement of the copper centers from the mean equatorial donor plane has been shown to have little effect on the exchange in other cases and is not expected to influence the exchange situation significantly in the systems under discussion.[30] The copper–nitrogen (diazine) bond lengths and bond angles might be expected to influence the exchange contribution from the diazine bridge itself. The average Cu–N distances (2.044, 2.043 Å) and Cu–N–N (diazine) angles (120.7, 120.8°) for XIII and XVI, respectively, show that this molecular framework is essentially the same for both $[Cu_2(MIP)(OH)Cl_3(H_2O)]\cdot H_2O$ and $[Cu_2(MIP)(OH)Br_3(H_2O)]\cdot H_2O$.[7,17] The average Cu–N distance (1.951 Å) is somewhat shorter for XV, but the average Cu–N–N angle (120.5°) is essentially the same. However, on the assumption that the diazine bridge provides a minor and roughly constant contribution to the total exchange, the differences can be associated with the peripheral donors, X (Table IV). These vary from Cl (XIII) to Br (XVI) to pyridine (XV), and since they are all bound in the equatorial planes of the two copper centers, they can be considered to have a significant influence on the metal magnetic orbitals. For compounds XIV and XVII a similar, marked increase in exchange is observed when bromide replaces chloride (ϕ = 7.73 and 11.1, respectively). It is well established that for symmetric halogen-bridged copper(II) dimers $-2J$ increases as Cl < Br[33] and this trend of an increased antiferromagnetic contribution with decreasing electronegativity of a bridging ligand has also been observed by Kahn et al. for binuclear copper(II) complexes bridged by oxalate, oxamide, and dithiooxamide ligands.[30] However for terminally bound groups such an effect has not been demonstrated, to our knowledge.

The axially bound halogen atoms are not expected to have any significant influence on the copper magnetic orbitals in compounds XIII, XIV, XVI, and XVII, from the standpoint of orbital symmetry and also because the bonding contacts to these atoms are so large. However the shorter in-plane halogen contacts are expected to influence the copper magnetic orbitals, but since they are bound terminally, then their major influence could be considered in terms of only how they would polarize the electron density in the copper–halogen bond. The less electronegative bromine atom would, therefore, be expected to polarize the electron density in this bond, and hence in the copper magnetic orbital, to a lesser extent than chlorine, thus effectively allowing more electron density in the copper magnetic orbital to participate in the exchange process with greater resulting exchange. The effect of replacing chlorine by bromine on exchange is also dramatically illustrated by comparing $[Cu_2(PTP)Cl_4]\cdot CH_3CH_2OH$ (II) ($-2J$ = 131 cm^{-1}) with the isostructural complex $Cu_2(PTP)Br_4$, for which the X-ray structure has been recently completed,[34] which has much larger exchange ($-2J$ = 243 cm^{-1}).

The major features that distinguish the phthalazine complexes XIII and XVI and the pyridazine complexes XIV and XVII include the fused benzene ring and the angle N(diazine)–Cu–O(H). For the pyridazine complexes this angle is around 90°, whereas for the phthalazine complexes XIII and XVI it is around 85°. While in-plane distortions at the copper centers characterize the structures of all these complexes,[17] it is this angle that may have a significant influence on the overall magnetic pathway connecting the two copper centers. The smaller angle in the case of the phthalazine derivatives XIII and XVI could well lead to diminished exchange via the diazine bridge in these compounds. Additional evidence to support this suggestion comes from complex XV, where angles of close to 90° exist, no doubt as a result of the geometrical influence of the hexadentate phthalazine ligand (ϕ = 8.44 versus ϕ = 6.10 and 7.94 for XIII and XVI, respectively). However, since the inplane donors for XV (N_3O) differ substantially from those in XIII and XVII (N_2OX; X = Cl, Br) the magnetic copper orbital will undoubtedly be influenced to a different extent in these two groups of compounds, which will have some effect, albeit probably small, on the exchange situation. The extended π-delocalization pathway present in the phthalazine entity should also be considered as a contributing factor to the general difference in exchange between the pyridazine and phthalazine complexes.

The major results that emerge from this magnetostructural study are that (1) the pyridazine bridge is a better superexchange medium than phthalazine, (2) terminal bromo derivatives have significantly enhanced exchange in comparison with structurally analogous chloro derivatives, (3) a planar, hexadentate phthalazine ligand generates a complex with a stronger apparent exchange than a comparable tetradentate ligand, and (4) the chelate ring size and the size of nonmagnetic bridge groups profoundly affect binuclear center dimensions, and hence exchange, in the case of hydroxo-bridged derivatives.

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Supplementary Material Available: Listings of anisotropic thermal parameters (Table SI), bond length and angle data pertaining to the ligand and the nitrate groups, respectively (Table SIII), and least-squares planes and deviations therefrom for IX (Table SIV) (19 pages); a listing of observed and calculated structure factors for IX (Table SII) (90 pages). Ordering information is given on any current masthead page.

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