2210 *Inorg. Chem.* **1992,** *31,* 2210–2214

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Binuclear Lead(II) and Copper(II) Complexes of 1,4-Dihydrazinophthalazine (DHPH). Stabilization of Copper(II) in the Presence of a Hydrazine Moiety and X-ray Crystal Structure and Magnetic Properties of $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$

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Received September 9, 1991

The tetradentate, binucleating ligand, 1,4-dihydrazinophthalazine (DHPH) does not form stable copper(II) complexes on direct reaction with copper(II) salts, because of its strongly reducing nature. However, binuclear copper(II) complexes of DHPH can be produced as relatively stable solid-state species by transmetalation of $[Pb_2(DHPH)_2(MeOH)_2(ClO_4)_2](ClO_4)_2$ (I) with copper(II) salts. The single-crystal X-ray structure of $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II) has been determined. $Cu_2C_{16}H_{24}N_{12}Cl_4O_{18}$ (II) crystallized in the triclinic system, space group $P\bar{1}$ with $a = 8.0732$ (22) Å, $b = 10.0881$ (19) Å, $c = 10.2377$ (24) Å, $\alpha = 97.357$ (18)°, $\beta = 99.960$ (22)°, $\gamma = 106.677$ (18)°, and one formula unit per unit cell. Refinement by full-matrix least squares gave final residuals $R = 0.068$ and $R_w = 0.051$. Each copper centre is bonded by four short planar contacts to ligand nitrogen atoms (Cu–N 1.96–2.02 Å) with longer axial contacts to water (2.351 Å) and a perchlorate oxygen (2.615 Å). II exhibits fairly strong intradimer antiferromagnetic coupling with $-2J = 489$ (1) cm^{-1}. A comparison of this complex with a structurally related binuclear copper pyridazine complex indicates a capacitor-like effect associated with the phthalazine–benzene ring, which leads to reduced spin-coupling for the phthalazine bridge.

Introduction

1,4-Dihydrazinophthalazine (DHPH) is potentially a tetradentate ligand capable of binding two metal ions simultaneously in close proximity. However its coordination chemistry has been limited to a few studies, in which binuclear nickel(II),[2–4] cobalt(II),[5] and molybdenum(IV)[6] complexes were examined. No examples of copper(II) complexes appear to have been studied, so far, because of the instability of copper(II) salts in the presence of the strongly reducing hydrazine ligand. However the high reactivity of the hydrazine residues has led to the synthesis of a number of open-chain, hexadentate Schiff-base ligands by reaction with aldehydes and ketones and their corresponding binuclear cobalt(II),[7] nickel(II),[7,8] and copper(II)[9–11] complexes and also mononuclear and polynuclear molybdenum derivatives.[12] Some binuclear, macrocyclic nickel(II)[13–15] and cobalt(II)[16] derivatives have also been synthesized by template condensation reactions involving dihaloalkanes, diketones etc.

Only one binuclear complex of DHPH has been structurally characterized. The antiferromagnetically coupled complex $[Ni(DHPH)(H_2O)_2]_2Cl_4{\cdot}2H_2O$ involves two octahedral nickel(II) centers bound simultaneously by two ligands, with the DHPH nitrogens providing two equatorial donors per nickel with water molecules occupying axial sites. Two diazine (N–N) groups bridge the nickel centers with a Ni–Ni separation of 3.79 Å.[3] In another, very unusual system, reaction of DHPH with $MoO_2Cl_2(DMF)_2$ (DMF = dimethylformamide) produces a binuclear Mo(IV) DHPH derivative, in which the ligand appears to have undergone an oxidative dehydrogenation to produce a quadruply deprotonated diazene ligand.[6] In general, reaction of DHPH with copper(II) salts produces dark brown products which seem to contain a mixture of species, including copper(I) derivatives and metallic copper, and in spite of great efforts no copper(II) complex of DHPH could be synthesized by a direct route. A similar instability with respect to copper(II) was reported for phthalazine–hydrazone ligands derived by reaction of DHPH with *p*-tolualdehyde and 2,5-dimethylbenzaldehyde. In these cases ligand hydrolysis led to the formation of hydrazine fragments which produced Cu(I) hydrazone complexes.[17]

In this study we report the synthesis and structural characterization of copper(II) and lead(II) complexes of DHPH. The olive-green copper(II) complex $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II) has been prepared by a transmetalation technique,[18] in which the binuclear lead(II) complex $[Pb_2(DHPH)_2(MeOH)_2(ClO_4)_2](ClO_4)_2$ (I) is reacted with copper(II) perchlorate in methanol. An X-ray crystal structure shows II to be a binuclear derivative involving pseudooctahedral copper(II) centers, structurally similar to the nickel derivative. The transmetalation technique produces other copper derivatives, but in most cases some ligand decomposition is observed, with loss of hydrazine fragments. Variable-temperature magnetic measurements on II indicate fairly strong intramolecular antiferromagnetic coupling ($-2J = 489$ (1) cm^{-1}), which, when compared with a structurally related pyridazine complex, supports previous observations that pyridazine-bridged complexes exhibit stronger antiferromagnetic exchange than related phthalazine complexes.[19,20] Also, within a group of related, diazine-bridged binuclear copper(II) complexes, which includes pyridazine, phthalazine, pyrazole, and triazole ligands, pyridazine emerges as the most efficient antiferromagnetic superexchange bridge.

Experimental Section

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. The complexes described in this report have, so far, been found to be safe when used in small quantities.

Synthesis of Complexes. $[Pb_2(DHPH)_2(MeOH)_2(ClO_4)_2](ClO_4)_2$ (I). A solution of DHPH[21] (0.20 g, 1.0 mmol) in hot methanol (125 mL) was added slowly to a solution of $Pb(ClO_4)_2{\cdot}6H_2O$ (1.0 g, 2.0 mmol) in methanol (25 mL). The mixture was refluxed for 30 min. A pale yellow

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Table I. Crystallographic Data for $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II)

chem formula: $Cu_2C_{16}H_{24}N_{12}Cl_4O_{18}$
fw = 937.3
space group: $P\bar{1}$
$a = 8.0732\ (22)$ Å
$b = 10.0881\ (19)$ Å
$c = 10.2377\ (24)$ Å
$\alpha = 97.357\ (18)°$
$\beta = 99.960\ (22)°$
$\gamma = 106.677\ (18)°$
$V = 772.6\ (3)$ Å^3
$Z = 1$

index ranges
  h, −8 to 8
  k, 0 to 10
  l, −10 to 10
$T = 22$ °C
$\lambda = 0.709\,30$ Å
$\rho_{calcd} = 2.015$ g cm^{-3}
$\mu = 1.82$ mm^{-1}
$R^a = 0.068$
$R_w{}^a = 0.051$

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

solid separated on cooling, which was filtered out and washed with methanol (3 × 10 mL) and dried in vacuo (yield: 75%). Anal. Calcd for $Pb_2(C_8H_{10}N_6)_2(CH_3OH)_2(ClO_4)_4$: C, 17.19; H, 2.23; N, 13.38; Pb, 33.0. Found: C, 17.05; H, 1.98; N, 13.62; Pb, 32.3.

$[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II). $[Pb_2(DHPH)_2(MeOH)_2(ClO_4)_2](ClO_4)_2$ (I) (0.5 g) was suspended in methanol (50 mL), and $Cu(ClO_4)_2\cdot 6H_2O$ (1.0 g, excess) was added. The reaction mixture was warmed on the steam bath and after about 5 min the lead complex dissolved, resulting in the formation of a bluish-green solution. The solution was filtered and allowed to stand at room temperature for 2 h, during which time olive green crystals formed (yield: 50%). Anal. Calcd for $Cu_2(C_8H_{10}N_6)_2(H_2O)_2(ClO_4)_4$: C, 20.42; H, 2.57; N, 17.86; Cu, 13.50. Found: C, 20.64; H, 2.56; N, 17.96; Cu, 13.80.

Physical Measurements. Room-temperature magnetic moments were measured by the Faraday method using a Cahn 7600 Faraday magnetic susceptibility system. Variable-temperature magnetic susceptibility data were obtained in the range 5–305 K by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T min^{-1} were employed.

Infrared spectra were recorded using a Mattson Polaris FTIR spectrometer and electronic spectra with a Cary 17 instrument. EPR spectra were recorded using a Bruker ESP 300 X-band spectrometer at room temperature and 77 K. Microanalyses were carried out by Canadian Microanalytical Service, Delta, Canada.

Crystallographic Data Collection and Refinement of the Structure. $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II). Crystals of II are olive green. The diffraction intensities of an approximately 0.10- × 0.15- × 0.35-mm crystal were collected with graphite-monochromatized Mo Kα radiation using an Enraf Nonius diffractometer and the $\theta/2\theta$ scan mode, with profile analysis[22] to $2\theta_{max} = 44.9°$. A total of 2801 reflections were measured, of which 2006 were unique and 1532 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 20 reflections with 2θ in range 35–45°.

The structure was solved by direct and difference Fourier methods using the NRCVAX crystal structure programs[23] and refined by full-matrix least-squares methods to final residuals of R and R_w of 0.068 and 0.051, respectively ($R = \sum(|F_o| - |F_c|)/\sum(|F_o|)$; $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w(|F_o|)^2]^{1/2}$) with weights based on counting statistics. In the last difference map the deepest hole was −0.74 e Å^{-3} and the highest peak 1.14 e Å^{-3}. Hydrogen positions were calculated. Scattering factors for neutral species were taken from ref 24. A summary of crystal data is given in Table I, and atomic coordinates are given in Table II. Anisotropic thermal parameters (Table SI) and a listing of structure factors are included as supplementary material.

Results

Description of the Structure of $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II). The structure of the cation in II is shown in Figure 1. Bond lengths and bond angles relevant to the copper coordination spheres are given in Table III. The triclinic unit cell contains a single binuclear cation $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2]^{2+}$, with a crystallographically imposed center of symmetry. The cation consists of two copper(II) ions bridged by the two phthalazine nitrogen atoms of the two DHPH ligands, with one water molecule and a distant, monodentate perchlorate oxygen completing a distorted octahedron at each copper center (the perchlorate ligand is not included in Figure 1). The DHPH molecules are essentially planar (the dihedral angle between the least-squares planes of the two phthalazine moieties is 0.00 (3)°) and behave as tetradentate bis chelate ligands, providing two basal

Table II. Final Atomic Positional Parameters and Equivalent Isotropic Debye–Waller Temperature Factors (Esd's) for $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II)

	x	y	z	B_{iso},^{a} Å^2
Cu	0.86384	0.31193	0.93538	2.52 (7)
Cl(1)	0.6994 (5)	−0.0561 (3)	0.3624 (4)	4.36 (19)
Cl(2)	0.2416 (5)	0.1990 (4)	0.0749 (4)	4.71 (21)
O(1)	0.5629 (10)	−0.0277 (8)	0.2692 (8)	4.3 (4)
O(2)	0.7047 (11)	−0.1921 (9)	0.3201 (9)	6.3 (6)
O(3)	0.8629 (12)	0.0397 (11)	0.3674 (12)	11.4 (8)
O(4)	0.6640 (16)	−0.0434 (13)	0.4947 (11)	11.4 (10)
O(5)	0.2965 (14)	0.1224 (10)	0.1603 (12)	11.2 (8)
O(6)	0.3685 (15)	0.3330 (11)	0.0923 (15)	13.4 (11)
O(7)	0.0924 (15)	0.2232 (14)	0.0832 (14)	13.3 (12)
O(8)	0.2205 (21)	0.1238 (18)	−0.0451 (17)	17.3 (6)
OW	0.6206 (10)	0.3827 (8)	0.8466 (7)	4.2 (4)
N(1)	0.8823 (10)	0.4273 (8)	1.1125 (8)	2.1 (4)
N(2)	0.7071 (11)	0.1634 (8)	1.0104 (8)	3.1 (5)
N(3)	0.7029 (11)	0.2190 (8)	1.1416 (9)	3.0 (5)
N(4)	1.0252 (10)	0.4299 (8)	0.8415 (8)	2.1 (4)
N(5)	0.8407 (11)	0.1647 (8)	0.7742 (8)	2.9 (5)
N(6)	0.9276 (11)	0.2305 (8)	0.6801 (8)	2.9 (5)
C(1)	0.7908 (14)	0.3574 (11)	1.1897 (10)	2.41 (23)
C(2)	0.7734 (14)	0.4189 (11)	1.3187 (10)	2.83 (24)
C(3)	0.6695 (14)	0.3433 (11)	1.3985 (10)	3.00 (25)
C(4)	0.6607 (14)	0.4102 (11)	1.5209 (11)	3.4 (3)
C(5)	1.2341 (15)	0.4421 (12)	0.4316 (11)	3.9 (3)
C(6)	1.1388 (14)	0.3696 (11)	0.5094 (11)	2.87 (24)
C(7)	1.1305 (14)	0.4364 (10)	0.6346 (10)	2.59 (23)
C(8)	1.0297 (13)	0.3680 (11)	0.7228 (10)	2.24 (22)

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

Table III. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres in $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2]^{2+}$ (II)

Cu–O(7)	2.615 (12)	Cu–N(2)	1.996 (8)
Cu–OW	2.351 (7)	Cu–N(4)	1.965 (8)
Cu–N(1)	1.981 (7)	Cu–N(5)	2.019 (7)
O(7)–Cu–OW	165.8 (3)	N(1)–Cu–N(2)	81.9 (3)
O(7)–Cu–N(1)	81.6 (3)	N(1)–Cu–N(4)	107.3 (3)
O(7)–Cu–N(2)	78.0 (4)	N(1)–Cu–N(5)	169.3 (3)
O(7)–Cu–N(4)	98.6 (4)	N(2)–Cu–N(4)	169.8 (3)
O(7)–Cu–N(5)	90.9 (4)	N(2)–Cu–N(5)	89.2 (3)
OW–Cu–N(1)	88.6 (3)	N(4)–Cu–N(5)	81.2 (3)
OW–Cu–N(2)	90.6 (3)		
OW–Cu–N(4)	94.0 (3)		
OW–Cu–N(5)	97.4 (3)		

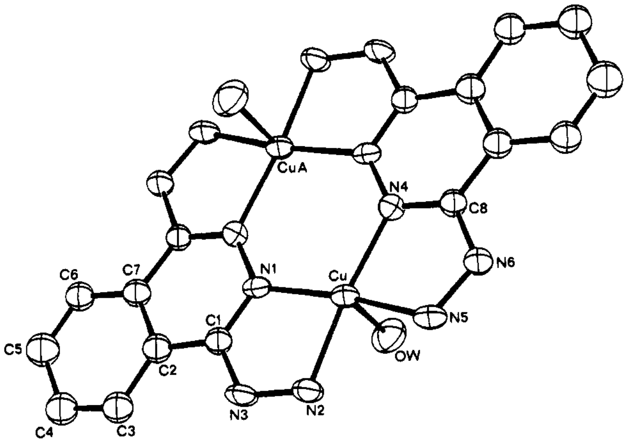

Figure 1. Structural representation of $[Cu_2(DHPH)(H_2O)_2]^{2+}$ (II) with hydrogen atoms omitted (40% probability thermal ellipsoids).

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nitrogen donor groups per metal center. Copper–nitrogen bond distances are close to 2.0 Å and slightly shorter than those found in the analogous nickel(II) derivative $[Ni_2(DHPH)_2(H_2O)_4]Cl_4\cdot 2H_2O$.[3] The axial Cu–O bond lengths of 2.351 Å (H_2O) and 2.615 Å (ClO_4^-) are considerably longer than those reported for the nickel complex (2.16 Å), and the copper center is displaced slightly (0.088 Å) from the mean N_4 plane toward the axial water molecule. Some N–Cu–N and O–Cu–N angles deviate substantially from the ideal octahedral value (90°) but are comparable with those reported for the analogous nickel complex.[3] Within each DHPH ligand the distances and angles are consistent with those found in the complex $[Ni_2(DHPH)_2(H_2O)_4]Cl_4\cdot 2H_2O$,[3] the only other structurally characterized complex of this ligand. The copper–copper separation (3.729 Å) is quite long, but comparable with the nickel–nickel separation of 3.791 Å found in the nickel chloride derivative.[3] The perchlorates are associated with the metal cation both through long-range contact between the copper and O(7) (2.615 Å) and through hydrogen bonds to OW and some nitrogen atoms. Equivalents of O(6) and O(2) $(1-x, 1-y, 1-z)$ are 2.834 and 2.869 Å from OW respectively and there are slightly longer contacts between O(5) and N(5) (2.940 Å) and O(1) and N(3) (2.985 Å).

Synthesis of the Complexes. The reaction of copper(II) salts with 1,4-dihydrazinophthalazine at ambient temperature or under reflux conditions, in various solvents, resulted in the formation of blackish-brown solids, of varying stoichiometry and with high metal content. No satisfactory characterization of these products could be obtained, and it was clear that, under these conditions, copper(II) complexes of DHPH could not be stabilized and significant decomposition occurred involving reduction of copper and ligand decomposition. A strategy involving the incorporation of DHPH fragments into a macrocyclic ligand involving template condensation with 2,6-diformyl-4-alkylphenols was then carried out, in an attempt to form a stable binuclear copper(II) complex based on DHPH. The same result was obtained with reduction of copper, ligand decomposition, and the formation of products with ill-defined composition. Clearly, the strongly reducing nature of the hydrazine ligand fragments is responsible for copper(II) reduction. Such reductions also occur with open-chain Schiff-base ligands derived from DHPH.[17]

In spite of this instability with respect to copper(II), it was felt that if the ligands could be assembled in an appropriate geometric arrangement around two non-transition-element atoms then a transmetalation reaction might successfully produce a binuclear copper(II) complex with DHPH. Reaction of a large excess of copper(II) perchlorate with the lead complex $[Pb_2(DHPH)_2(MeOH)_2(ClO_4)_2](ClO_4)_2$ (I) in methanol produced the relatively stable green copper(II) complex $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II). However the green mother liquor from this reaction deposited a small quantity of golden yellow needles on standing for a few days, which were identified as a mononuclear complex with the composition $Cu(C_8H_6N_2)_2(ClO_4)_2$ (III) (Anal. Calcd for $Cu(C_8H_6N_2)_2(ClO_4)_2$: C, 36.74; H, 2.30; N, 10.72. Found: C, 36.23; H, 2.20; N, 10.79). DHPH appears to have lost two hydrazino fragments, with the resulting formation of the ligand phthalazine. This would be expected to lead to some copper(II) reduction, but no reduced species were isolated.

Spectral and Magnetic Properties. Reaction between $Pb(ClO_4)_2$ and DHPH in methanol produced a pale yellow complex with a 1:1 metal:ligand stoichiometry (I). This complex has been assigned a binuclear structure similar to II and the nickel complex $[Ni_2(DHPH)_2(H_2O)_4]Cl_4\cdot 2H_2O$. A strong infrared absorption at 3551 cm^{-1} is consistent with the presence of coordinated methanol, and a broad, strong absorption with major components at 1094 and 1001 cm^{-1} suggests weak, axial association of a monodentate perchlorate, indicating the presence of six-coordinate lead(II) ions. A strong absorption at 3302 cm^{-1}, which does not show any change from its position in the free ligand, is assigned to secondary NH, while absorptions at 3222 and 3182 cm^{-1} are assigned to the coordinated NH_2 group. In the free ligand this absorption appears as a broad band at 3211 cm^{-1}.

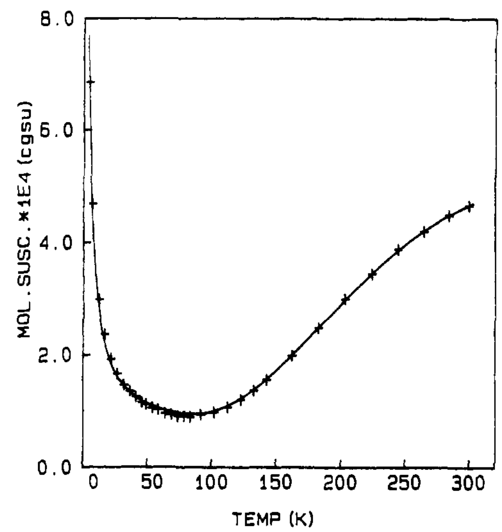


Figure 2. Magnetic data for $[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II). The solid line was calculated from eq 1 with $g = 2.083$ (6), $-2J = 489$ (1) cm^{-1}, and $\rho = 0.0070$.

$[Cu_2(DHPH)_2(H_2O)_2(ClO_4)_2](ClO_4)_2$ (II) exhibits two sharp absorptions in the infrared at 3551 and 3487 cm^{-1}, associated with coordinated water, and strong sharp bands at 3340, 3269, and 3193 cm^{-1}, associated with NH and NH_2 groups. A strong, broad perchlorate absorption, centered at 1088 cm^{-1}, has no significant splitting, suggesting that, although the Cu–O(7) distance of 2.615 Å is considered to be a weak bonding contact, significant lowering of the tetrahedral symmetry of the perchlorate ion is not reflected in the infrared spectrum. The low room-temperature magnetic moment (1.04 μ_B) for II is clearly indicative of moderately strong antiferromagnetic coupling in the binuclear center.

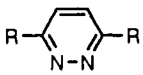
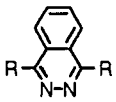
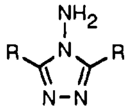
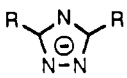
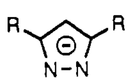
The yellow mononuclear complex $Cu(C_8H_6N_2)_2(ClO_4)_2$ (III) shows no NH stretching absorption in the infrared around 3200 cm^{-1} or in the NH deformation region around 1630 cm^{-1} (the other complexes containing DHPH have strong infrared absorptions in this region associated with NH deformation), indicating the absence of hydrazine fragments in the new ligand. A reasonable ligand fragment based on analytical and infrared data is therefore phthalazine itself. Splitting of the ν_3, perchlorate vibrations, with major components at 1076 and 1042 cm^{-1}, suggests the possibility of monodentate perchlorate and the probability of a simple, square-planar CuN_2O_2 structure for III. A room-temperature magnetic moment of 1.86 μ_B supports the mononuclear nature of this complex.

The solid-state X-band ESR spectrum of II at room temperature exhibits a half-field ($\Delta M_s = \pm 2$) signal ($g = 4.36$), typical of a spin-coupled binuclear copper(II) system with significant population of the triplet state. At low temperature (77 K), however, the signal disappears. A broad $\Delta M_s = \pm 1$ transition is also observed at $g = 2.090$, which is presumably due to a monomeric impurity. Two major absorptions are observed in the solid-state (mull transmittance) electronic spectrum for II at 18 200 and 24 100 cm^{-1}, assigned to d–d and charge-transfer transitions, respectively.

Variable-temperature magnetic data have been obtained for a freshly prepared sample of II in the temperature range 5–305 K. The experimental data (Figure 2) are typical of a binuclear copper(II) complex with moderately strong intramolecular antiferromagnetic exchange, with the presence of a small amount of a monomeric, paramagnetic impurity, as indicated by the rise in susceptibility at low temperatures. The data have been fitted to the Bleaney–Bowers expression (eq 1)[25] using the isotropic

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

Table IV. Magnetic Data for Diazine-Bridged (Cu_2N_8) Binuclear Copper Complexes

diazine bridge	$-2J$, cm^{-1}	ref
	536 (2)[a] 545 (4)[b] 479 (1)[c]	26
	489 (1)[d]	this work
	200–244[e]	29
	204–236[f]	30
	241 (3), 244 (3)[g] 270[h] 428,[i] 362[j]	31 32 33

[a] R = –CR′═N—OH (R′ = H). [b] R = –CR′═N—OH (R′ = Ph). [c] R = –S—py. [d] R = $NHNH_2$. [e] R = $-CH_2NH_2$. [f] R = py. [g] R = H. [h] R = H. [i] R = $-CH_2NH(CH_2)_2NEt_2$. [j] R = $-CH_2NH(CH_2)_3NMe_2$.

(Heisenberg) exchange Hamiltonian ($\mathcal{H} = -2JS_1 \cdot S_2$) for two interacting $S = {}^1/_2$ centers (χ_m is expressed per mole of copper atoms, $N\alpha$ is the temperature-independent paramagnetism, set at 60×10^{-6} cgsu for copper, and ρ = fraction monomeric impurity). A nonlinear regression analysis of the data was carried out with ρ as a floating parameter. The best-fit line is shown in Figure 2 for $g = 2.083$ (6), $-2J = 489$ (1) cm^{-1}, $\rho = 0.0070$ ($10^2R = 0.53$; $R = [\sum(\chi_{obs} - \chi_{calcd})^2/\sum(\chi_{obs})^2]^{1/2}$). The g value is comparable with that obtained from the ESR spectrum. The application of a Weiss correction did not improve the data fit, indicating no intermolecular exchange coupling. Additional variable-temperature magnetic data were obtained on a total of four samples of II, prepared independently and measured over a period of 12 days. The average value of $-2J$ was found to be 489 cm^{-1}, with the paramagnetic impurity fraction increasing from approximately 0.0001 to 0.008. These observations are consistent with the fact that the complex is inherently unstable.

Spin-coupling between the copper(II) centers is quite strong and occurs through a superexchange mechanism via the diazine bridges. The flat nature of the binuclear cation clearly leads to very effective overlap of the copper $d_{x^2-y^2}$ magnetic orbitals with the appropriate orbitals on the phthalazine bridge. In our previous studies on the magnetostructural properties of pyridazine- and phthalazine-bridged binuclear copper(II) complexes, we concluded that antiferromagnetic coupling was generally stronger via a pyridazine bridge than via a phthalazine bridge, and this was attributed to the fact that metal ion charge could be delocalized into the fused benzene ring of the phthalazine moiety.[19,20] Fortuitously, the recent report of the structural and magnetic properties of the related and directly relevant complex $[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2](HL^1$ = μ-(pyridazine-3,6-dicarbaldehyde dioximate)) (Table IV; footnotes a and b) allows a very realistic comparison to be made between the exchange capacities of the phthalazine and pyridazine bridges.[26] The pyridazine derivative has a planar, binuclear six-coordinate structure, with four in-plane nitrogen donors per metal, which is exactly analogous to that of II, with comparable in-plane Cu–N distances and angles and axial contacts to a water (Cu–OW 2.310 (6) Å) and perchlorate (Cu–O 2.554 (6) Å). Variable-temperature magnetic studies in the range 20–292 K for this complex indicate moderately strong antiferromagnetic exchange with $g = 2.12$ (2) and $-2J = 536$ (2) cm^{-1}. A structurally related complex involving the ligand 3,6-dibenzoylpyridazine dioximate was shown to exhibit slightly stronger antiferromagnetic coupling ($-2J = 545$ (4) cm^{-1}).[26] The close structural comparison between II and the pyridazine dioximate complexes, involving almost identical, distorted six-coordinate copper ion chromophores and ignoring any small electronic perturbations associated with slight differences in the diazine side chains, clearly suggests that the absence of the fused benzene ring, with its capacitor-like action for delocalized metal unpaired spin, allows for a more efficient antiferromagnetic interaction between the two copper(II) centers in the pyridazine complexes, as illustrated by the larger $-2J$ values.

The planar nature of both the phthalazine and pyridazine dimers and Cu–N–N in plane angles close to 120° (average 126.1° in II and 127.5° in the pyridazine dimer) would suggest very efficient overlap between the copper magnetic orbitals and the diazine bridge. This planarity is associated with the presence of terminal five-membered chelate rings in both cases. However the introduction of an extra atom in the terminal ligand grouping, for example in the ligand 3,6-bis(2′-pyridylthio)pyridazine (PTP) (Table IV, footnote c) produces, in one case at least, a nonplanar dimeric structure. The complex $[Cu_2(PTP)_2Cl](ClO_4)_3$ involves two square-pyramidal copper centers bridged equatorially by two pyridazines and bridged axially by a chlorine.[27] The copper basal planes are canted toward each other with a dihedral angle of 76.9° and twisted significantly relative to the pyridazine planes, such that the $Cu_2(N_2)_2$ ring adopts a boat conformation. The dihedral angle between the pyridazine planes is 92.1°. Antiferromagnetic coupling in this case ($-2J = 479$ cm^{-1}) is significantly less than that occurring in the pyridazine dioximate complexes, which can be associated with the electron-withdrawing axial chlorine[20,28] and the nonplanar nature of the Cu_2N_4 bridge framework. Surprisingly, the exchange efficiency of the diazine bridge does not appear to be markedly impaired by what is a very significant twist of the copper planes relative to the pyridazine planes.

Magnetic studies on other Cu_2N_8 diazine systems, in which the copper(II) centers are bridged only be neutral diazine moieties are rare. A binuclear copper(II) complex of the ligand aamt (Table IV, footnote e), $[Cu(aamt)Br(H_2O)]_2Br_2(H_2O)_2 \cdot CH_3OH$,[29] involves a planar bis(ligand) structure related to II, with a Cu–Cu separation of 4.0694 (7) Å. In a series of structurally related complexes of aamt, exchange integrals ($-2J$) fall in the range 200–224 cm^{-1}, indicating much weaker antiferromagnetic exchange than occurs in II. The absence of a fully delocalized ring π system and the presence of other nitrogen atoms within the triazole group clearly diminish antiferromagnetic exchange. The five-membered triazole ring also has the effect of forcing the metal centers further apart (than in II), with the result that Cu–N–N angles (134.2 and 133.7°) are somewhat larger than those found in II (127.5 and 124.7°). However these differences in bridge angle might not be expected to cause such a large difference in exchange. Another related triazole ligand, bpt (Table IV, footnote f) forms the 1:1 binuclear, square-pyramidal, triazolate-bridged copper(II) complex $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$. This compound has a fairly flat, $Cu_2(N_2)_2$, diazine chelate ring and copper–copper separations and diazine bridge angles similar to those found in the aamt complex.[30] Exchange integrals ($-2J$) for a series of structurally related bpt complexes fall in the range 204–236 cm^{-1}, indicating a similarity in the superexchange capacity of the triazolate bridge and the neutral amino–triazole bridge.

The bis(μ-pyrazolato)-bridged complexes $[Cu_2(H_2B(pz)_2)_2(pz)_2Cl](PPh_4) \cdot 0.5(CH_3)_2CO$ and $[Cu_2(H_2B(pz)_2(pz)_2Br](AsPh_4) \cdot (CH_3)_2CO$ involve a pair of square-pyramidal copper(II) centers bridged equatorially by just pyrazolates (pz) and axially by a halogen (Table IV, footnote g). The copper square pyramids

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are canted in a boat conformation, with a relatively short copper–copper separation (3.387 (6) Å) in the chloro derivative,[31] and a long axial contact (2.566 (4) Å). Both complexes are antiferromagnetically coupled with $-2J$ = 241 and 244 cm^{-1}, respectively. The similarity in exchange coupling between the planar triazolate-bridged and the canted pyrazolate-bridged derivatives may be fortuitous but may be a reflection on the combined effects of nonplanarity of both the pyrazolate planes and the copper coordination planes, as indicated by theoretical MO studies.[31] In this case the dihedral angle between the pyrazole planes is 93° while that between the CuN_4 planes is 104°. The presence of the electronegative, axial halogens must also be considered as an electronic perturbation on the electron density distribution in the magnetic molecular orbital arrangement linking the two copper centers. Previous studies have shown that both terminal and bridging chlorines can significantly reduce antiferromagnetic coupling between bridged copper(II) centers.[20,28]

In another, square-planar binuclear copper(II) complex involving a nonbridging macrocyclic ligand derived by template condensation of 1,3-diaminopropane and diformylfuran and just two pyrazolate bridges, the binuclear center is somewhat flatter with an angle of 145.2° between the pyrazole planes and 94.9° between the CuN_4 planes[32] (Table IV, footnote h). Antiferromagnetic exchange in this system ($-2J$ = 270 cm^{-1}) is significantly larger, indicating that as the pyrazole plane dihedral angles increase, antiferromagnetic exchange increases, in agreement with theoretical predictions.[31] An essentially planar Cu_2N_8, pyrazolate-bridged binuclear center exists in the complex $[Cu_2(L1)_2](BPh_4)_2$ (Table IV, footnote i), with a copper–copper separation of 3.903 (2) Å and diazine bridge angles of 130.6 (3) and 131.0 (2)°.[33] A similar structure is anticipated for the complex $[Cu_2(L2)_2](BPh_4)_2$ (Table IV, footnote j). Both of these complexes exhibit moderately strong antiferromagnetic coupling (Table IV), with $-2J$ values which are much larger than those for the nonplanar pyrazolate-bridged dimers, further substantiating the theoretical predictions that antiferromagnetic exchange should increase as the bridging arrangement approaches coplanarity.[31]

Conclusion

For the first time a relatively stable binuclear copper(II) complex of the potentially reducing hydrazine ligand DHPH has been synthesized by a transmetalation technique from the corresponding lead complex. The complex exhibits moderately strong antiferromagnetic coupling ($-2J$ = 489 (1) cm^{-1}), propagated by a superexchange mechanism through the phthalazine bridge. A comparison of two structurally related, essentially planar, pyridazine- and phthalazine-bridged binuclear complexes with equivalent in-plane N_8 donor sets shows that the pyridazine bridge is a more effective antiferromagnetic, superexchange pathway. The reduced exchange capacity of the phthalazine bridge is attributed to a capacitive charge storage effect associated with the fused benzene ring, which has also been observed in other studies.[19,20] By comparison of planar binuclear (1:1) copper(II) complexes with different diazine bridges, the neutral pyridazine bridge is more effective at propagating antiferromagnetic superexchange than phthalazine, triazole, triazolate, or pyrazolate bridges, in structurally related complexes. Of the five-membered ring diazine bridges it is apparent that pyrazolate has the capacity to propagate antiferromagnetic exchange more efficiently than triazole or triazolate, which can be associated with the presence of the extra electronegative nitrogen atom in the triazole ring, which has the ability to polarize spin within the triazole ring itself and thus limit exchange.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support for this study and Punjabi University, Patiala, for granting leave of absence to S.S.T.

Registry No. I, 140677-38-9; II, 140677-40-3; III, 140677-41-4.

Supplementary Material Available: Table SI, listing thermal parameters, Table SII, listing interatomic distances and angles, and Table SIII, listing calculated hydrogen atom positional parameters, and Figure S1, depicting a packing diagram for II (5 pages); a table of calculated and observed structure factors for II (11 pages). Ordering information is given on any current masthead page.

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