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Binuclear copper(II) complexes of some sexadentate phthalazine-hydrazone ligands with strong antiferromagnetic exchange*

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Abstract

Sexadentate phthalazine-hydrazone ligands (N_6), involving pyridine and *N*-methylimidazole as peripheral donor groups, form binuclear hydroxo-bridged copper(II) complexes which exhibit very strong antiferromagnetic exchange ($-2J = 885$–1211 cm^{-1}), which is propagated via a superexchange mechanism through the bridging diazine (N–N) and hydroxide groups. When the hydroxide bridge in $[Cu_2(APHP{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (APHP = 1,4-dihydrazinophalazine-bis(2-pyridine) acetaldimine) ($-2J = 988$ cm^{-1}) is replaced by a pyrazolide bridge, a dramatic decrease in exchange is observed ($-2J = 521$ cm^{-1}) indicating the importance of hydroxide as a dominant superexchange bridge. The complexes are highly colored, exhibiting very intense visible absorptions (16 400–16 700 cm^{-1}) associated with charge transfer transitions. The crystal and molecular structure of $[Cu_2(APHP{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (**VI**) is reported. **VI** crystallized in the monoclinic system, space group $P2_1/n$, with $a = 8.0110(20)$, $b = 24.100(5)$, $c = 15.6750(20)$ Å, $\beta = 100.240(20)°$ and four formula units per unit cell. Refinement by full-matrix least-squares gave final residuals of $R = 0.076$ and $R_w = 0.038$. This complex has a hydroxo-bridged square-pyramidal structure with a Cu–Cu separation of 3.296(2) Å and a Cu–O(H)–Cu angle of 117.8(3)°.

Introduction

The diazine (N–N) fragment forms the binucleating focus in binuclear complexes of a variety of substituted hydrazine [1–7], pyridazine [8–24], phthalazine [8, 9, 17, 19, 20, 25–44], pyrazole [8], and triazole [45–48] ligands. We have focussed our attention on tetradentate (N_4) [27, 29, 30, 32–44] and sexadentate (N_6) [44] phthalazine ligands and tetradentate pyridazine (N_4) ligands [17–24], which form predominantly hydroxide bridged copper(II) complexes, with copper–copper separations in the range 3.0–3.5 Å, and exhibit moderate to strong antiferromagnetic exchange between the copper(II) centres ($-2J = 190$–1304 cm^{-1}) [17, 18, 21, 22, 24, 27, 37, 40, 41, 43, 44, 49] for systems with hydroxide bridge angles and in the range 100.0–126.3°. A preliminary study of the structural and magnetic properties of the square-pyramidal, binuclear complex $[Cu_2(APHP{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (VI) (APHP = 1,4-dihydrazinophthalazine-bis(2-pyridine)acetaldimine (Fig. 1)) has already been reported [43].

In the present study we report full details of the structure of the complex $[Cu_2(APHP{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (VI), in addition to its magnetic properties and also the result of an examination of the magnetic properties of copper(II) perchlorate complexes of other related, substituted hydrazinophthalazine ligands (Fig. 1). Structurally all the complexes appear to be similar, with the two copper(II) centres bound to the sexadentate ligand with three nitrogen donors per metal and bridged by hydroxide (or pyrazole) and the phthalazine (N_2) group. $[Cu_2(APHP{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (Fig. 2) has a square-pyramidal structure with a Cu–Cu separation of 3.296(2) Å and a Cu–O(H)–Cu bridge angle of 117.8(3)°, relatively short in plane contacts (CuN_3O) and longer contacts to the axial water molecules. Very low room temperature magnetic moments signal strong antiferromagnetic ex-

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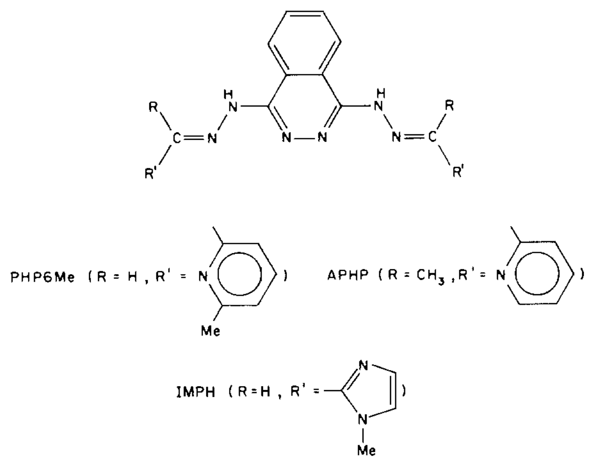

Fig. 1. Sexadentate phthalazine-hydrazone ligands.

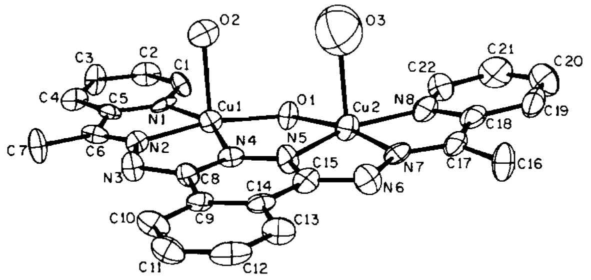

Fig. 2. Structural representation of $[Cl_2(APHP–H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (VII) with hydrogen atoms omitted (40% probability thermal ellipsoids).

change between the copper ions and variable temperature magnetic data indicate that exchange integrals ($-2J$) for selected compounds fall in the range 520–1211 cm^{-1}.

Experimental

Synthesis of ligands and copper complexes

IMHP [39] and APHP [44] were prepared as reported previously. PHP has been reported previously [3, 39], but in both cases was generated *in situ* and not isolated. This ligand was synthesized and isolated as follows.

1,4-dihydrazinophthalazine (DHPH) [50] (3.8 g, 20 mmol) and pyridine-2-carboxaldehyde (4.3 g, 40 mmol) were reacted in ethanol (60 ml) under reflux for 3 h, during which time the DHPH dissolved. On cooling yellow–brown crystals deposited, which were filtered off, washed with ethanol and petroleum ether (40/60) and dried in air (yield 45%; m.p. 240 °C). *Anal.* Calc. for $C_{20}H_{16}N_8$: C, 65.22; H, 4.34; N, 30.43. Found: C, 64.92; H, 4.41; N, 30.17%. PHP6Me was prepared in a similar manner and obtained as orange crystals (yield 40%; m.p. 160 °C. *Anal.* Calc. for $C_{22}H_{20}N_8 \cdot 2H_2O$: C, 61.11; H, 5.55; N, 25.93. Found: C, 60.93; H, 5.57; N, 25.62%.

$[Cu_2(IMHP)(OH)(H_2O)_2](ClO_4)_3 \cdot CH_3OH$ (**I**) [39] and $[Cu_2(PHP)(OH)](ClO_4)_3 \cdot 0.25CH_3CH_2OH$ (**II**) [39] were used as prepared previously.

$[Cu_2(PHP6Me–H)(OH)](ClO_4)_2 \cdot 0.5H_2O$ (IV)

PHP6Me (0.50 g, 1.3 mmol) was dissolved in hot methanol (75 ml) and added slowly to a hot solution of $Cu(ClO)_4)_2 \cdot 6H_2O$ (1.0 g, 2.7 mmol) dissolved in methanol (75 ml). A deep red–brown color resulted followed by the formation of a red–brown crystalline product, which was separated by filtration, washed with methanol/petroleum ether (40/60) and dried in air (yield 0.70 g). *Anal.* Calc. for $[Cu_2(C_{22}H_{19}N_8)(OH)](ClO_4)_2) \cdot 0.5H_2O$: C, 35.29; H, 2.94; N, 14.97. Found: C, 35.37; H, 2.81; N, 14.96%.

$[Cu_2(APHP)(OH)](ClO_4)_3$ (V)

APHP (0.40 g, 1.0 mmol) was dissolved in hot methanol (60 ml) and a methanolic solution (10 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.1 g, 3.0 mmol) added with stirring. On cooling to room temperature a brown crystalline product was obtained, which was filtered off, washed with ethanol and air dried (yield 0.40 g). *Anal.* Calc. for $[Cu_2(C_{22}H_{20}N_8)(OH)](ClO_4)_3$: C, 31.48; H, 2.39; N, 13.36. Found: C, 31.73; H, 2.57; N, 13.36%.

$[Cu_2(APHP–H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (VI)

APHP (0.12 g; 0.30 mmol) was dissolved in hot methanol (100 ml) and the solution cooled to room temperature. An aqueous solution (3 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.22 g; 0.60 mmol) was added and the mixture stirred and allowed to stand overnight. Brown crystals formed which were filtered off, washed with ethanol and air dried (yield 0.21 g). $[Cu_2(PHP–H)(OH)(H_2O)_2](ClO_4)_2$ (**III**) was prepared in a similar manner. *Anal.* Calc. for $[Cu_2(C_{22}H_{19}N_8)(OH)(H_2O)_2] \cdot (ClO_4)_2 \cdot H_2O$ (VI): C, 34.02; H, 3.35; N, 14.43. Found: C, 34.07; H, 3.06; N, 14.35%. *Anal.* Calc. for $[Cu_2(C_{20}H_{15}N_8)(OH)(H_2O)_2](ClO_4)_2$ (III): C, 32.17; H, 2.68; N, 15.01. Found: C, 32.23; H, 2.49; N, 14.91%.

$[Cu_2(APHP–2H)(OH)(H_2O)_2](ClO_4) \cdot 2H_2O$ (VII)

APHP (0.24 g, 0.60 mmol) was dissolved in hot methanol (200 ml). An aqueous solution (4 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.45 g, 1.2 mmol) was then added to the hot ligand solution followed by triethylamine (0.18 g; 1.8 mmol) dissolved in methanol (10 ml) and the mixture stirred. A dark, almost black, microcrystalline product was obtained, which was filtered off, washed with ethanol and air dried (yield 0.25 g). *Anal.* Calc. for $[Cu_2(C_{22}H_{18}N_8)(OH)(H_2O)_2](ClO_4)\cdot 2H_2O$: C, 37.18; H, 3.66; N, 15.77. Found: C, 37.05; H, 3.15; N, 15.63%.

[Cu₂(APHP-H)(Pyz)](ClO₄)₂ (VIII)

VI (0.16 g, 0.20 mmol) was dissolved in hot methanol (400 ml), under nitrogen, and the solution filtered. A methanolic solution (5 ml) of pyrazole (0.014 g, 0.20 mmol) was added and the mixture allowed to stand at room temperature overnight. On reducing the solution volume to 50 ml a brown crystalline product was obtained, which was filtered off, washed with ethanol and dried in air (yield 0.12 g). *Anal.* Calc. for $[Cu_2(C_{22}H_{19}N_8)(C_3H_3N_2)](ClO_4)_2$: C, 38.07; H, 2.79; N, 17.77. Found: C, 38.18; H, 2.92; N, 17.64%.

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 5–300 K (compounds **I–V**, **VII**, **VIII**) 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 m^{-1} were employed.

Infrared spectra were recorded using a Perkin-Elmer 283 and electronic spectra with a Cary 17. Conductance measurements were obtained using a General Radio Company bridge with impedance comparator and a constant temperature bath adjusted to 25 °C. Microanalyses were carried out by Canadian Microanalytical Service, Vancouver.

TABLE 1. Crystallographic data for $[Cu_2(APHP\text{-}H)(OH)(H_2O)_2](ClO_4)_2\cdot H_2O$ (**VI**)

Chemical formula	$Cu_2C_{22}H_{26}Cl_2N_8O_{12}$
Formula weight	792.49
Space group	$P2_1/n$
a (Å)	8.0110(20)
b (Å)	24.100(5)
c (Å)	15.6750(20)
β (°)	100.240(20)
V (Å^3)	2978.09
Z	4
T (°C)	22
λ (Å)	0.70930
ρ_{calc} (g cm^{-3})	1.77
μ (mm^{-1})	1.68
R	0.076
R_w	0.038
Octants of data collected (h, k, l)	−9 to 1, 0 to 25, 16 to −16
Equiv. reflections agreement	0.061

TABLE 2. Final atomic positional parameters and equivalent isotropic Debye–Waller temperature factors for $[Cu_2(APHP\text{-}H((OH)(H_2O)_2](ClO_4)_2\cdot H_2O$ (**VI**) with e.s.d.s in parentheses

	x	y	z	B_{iso}[a]
Cu1	0.33893(17)	0.12039(6)	0.82399(9)	3.10(7)
Cu2	0.18433(17)	0.11061(7)	1.00472(9)	3.55(8)
Cl1	0.7432(6)	0.23981(16)	0.0720(3)	8.0(3)
Cl2	0.8156(4)	0.07761(15)	0.43767(21)	5.64(21)
O1	0.3748(8)	0.1267(3)	0.9467(4)	3.5(4)
O2	0.2308(9)	0.2092(3)	0.7981(5)	4.9(5)
O3	0.0907(16)	0.2066(6)	0.9747(7)	15.8(11)
O4	0.3360(18)	0.2756(5)	0.9338(10)	19.0(13)
O5	0.6736(11)	0.1895(4)	0.0395(5)	7.8(6)
O6	0.6328(16)	0.2811(5)	0.0860(10)	18.7(12)
O7	0.8437(18)	0.2320(5)	0.1496(7)	19.3(12)
O8	0.8254(17)	0.2630(7)	0.0194(9)	21.5(14)
O9	0.9225(11)	0.0991(7)	0.4987(7)	17.6(11)
O10	0.6982(13)	0.0573(7)	0.4703(6)	18.3(13)
O11	0.8551(16)	0.0462(5)	0.3797(9)	19.4(13)
O12	0.7476(22)	0.1173(6)	0.3886(9)	22.9(16)
N1	0.5499(10)	0.1431(3)	0.7776(5)	3.1(5)
N2	0.2712(9)	0.0972(4)	0.7032(5)	2.9(5)
N3	0.1205(10)	0.0694(4)	0.6787(5)	3.5(5)
N4	0.1233(10)	0.0802(4)	0.8257(5)	3.0(5)
N5	0.0702(10)	0.0774(4)	0.9008(5)	3.0(5)
N6	−0.1387(11)	0.0548(4)	0.9800(5)	4.1(6)
N7	−0.0242(10)	0.0819(4)	1.0409(5)	3.2(5)
N8	0.2351(10)	0.1303(4)	1.1279(5)	3.6(5)
C1	0.6907(13)	0.1691(5)	0.8223(6)	3.1(6)
C2	0.8195(12)	0.1842(5)	0.7798(7)	3.7(7)
C3	0.8014(13)	0.1777(5)	0.6944(7)	4.5(8)
C4	0.6608(13)	0.1511(5)	0.6456(7)	3.4(7)
C5	0.5311(13)	0.1341(4)	0.6881(6)	3.3(6)
C6	0.3703(12)	0.1065(5)	0.6495(6)	3.3(6)
C7	0.3413(13)	0.0935(6)	0.5565(6)	4.3(7)
C8	0.0460(13)	0.0606(5)	0.7520(6)	3.2(6)
C9	−0.1187(12)	0.0332(4)	0.7480(7)	2.8(6)
C10	−0.2036(13)	0.0106(5)	0.6725(7)	3.9(7)
C11	−0.3588(14)	−0.0136(5)	0.6756(7)	4.9(7)
C12	−0.4216(13)	−0.0158(5)	0.7520(8)	4.6(8)
C13	−0.3399(13)	0.0050(5)	0.8281(7)	4.2(7)
C14	−0.1791(13)	0.0321(4)	0.8257(7)	3.1(6)
C15	−0.0842(12)	0.0541(5)	0.9033(6)	3.2(6)
C16	−0.1985(15)	0.0717(5)	1.1477(7)	5.1(8)
C17	−0.0399(13)	0.0910(5)	1.1182(6)	3.4(6)
C18	0.1054(13)	0.1199(5)	1.1716(6)	3.6(6)
C19	0.1144(14)	0.1338(5)	1.2573(6)	4.3(7)
C20	0.2508(16)	0.1594(6)	1.3017(7)	5.6(8)
C21	0.3824(15)	0.1710(5)	1.2587(7)	5.5(8)
C22	0.3662(14)	0.1564(5)	1.1737(7)	4.4(7)

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

Crystallographic data collection and refinement of the structure

$[Cu_3(APHP\text{-}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (VI)

Crystals of VI have a needle shape and are brown. The diffraction intensities of an approximately $0.10 \times 0.10 \times 0.30$ mm crystal were collected with graphite-monochromatized Mo Kα radiation using a Nonius diffractometer and the $\theta/2\theta$ scan mode, with profile analysis [51], to $2\theta_{max} = 44°$. A total of 4549 reflections was measured of which 3887 were unique and 2269 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 25 reflections with 2θ in the range 40–45°.

The structure was solved by direct and difference Fourier methods using the NRCVAX crystal structure programs [52] and refined by full matrix least-squares methods to final residuals of R and R_w of 0.076 and 0.038 respectively ($R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $R_w = [\Sigma w(|F_o| - |F_c|^2/\Sigma w(|F_o|)^2]^{1/2}$) with weights based on counting statistics. The final difference map had no peaks greater than 1.01 e A^{-3}. Hydrogen atoms on the aromatic rings (same number as the corresponding carbon atom) were added at calculated positions and then allowed to refine. All remaining hydrogen atoms (the two methyl groups (H5, H6, H7 attached to C7 and H14, H15, H16 attached to C16), the hydroxo-bridge (H9) and the one attached to N3 (H8)) were located from a subsequent difference map. The hydrogen atoms of the three water molecules (H17, H18 attached to O2, H23, H24 attached to O3 and H25, H26 attached to O4) were also included, at calculated positions, based on the hydrogen bonded network, but were not refined. Scattering factors for neutral species were taken from ref. 53. A summary of crystal data is given in Table 1, and atomic coordinates are given in Table 2. See also ' Supplementary material'.

Results and discussion

In the series of related compounds V, VI and VII the ligand behaves as a neutral monoanionic and dianionic species, respectively. The synthetic conditions that differentiate these systems involve the dilution conditions used during synthesis and the presence or absence of a base, e.g triethylamine. Reaction of the ligand APHP with copper perchlorate in small volumes of hot methanol causes the rapid formation of the neutral ligand, triperchlorate derivative (V), while the use of larger solvent volumes leads to the monoanionic ligand derivative (VI), in which proton loss has occurred. Clearly one exocyclic NH proton is very labile and can be removed under what are, at best, relatively mild basic conditions. Removal of both exocyclic NH protons requires the presence of a base and can be effected by the use of triethylamine. The conductance data for these compounds in DMF (Table 3) is entirely consistent with the proposed nature of their complex cations. Complexes I–IV were prepared using similar synthetic criteria and conductance data in DMF indicate 1:3 and 1:2 electrolytes, respectively, for these neutral and monoanionic ligand derivatives (Table 3). The formation of the pyrazolide derivative (VIII) involves the displacement of the hydroxide bridge in VI, which acts as a base, deprotonating the neutral pyrazole molecule. Conductance data indicate this species to be a 1:2 electrolyte in DMF.

The complex $[Cu_2(APHP\text{-}H)(OH)(H_2O)_2]$-$(ClO_4)_2 \cdot H_2O$ (VI) has a binuclear structure (Fig. 2) involving an almost planar, sexadentate ligand with the two square-pyramidal copper(II) centres bridged by the diazine nitrogen pair and a hydroxide [44]. Interatomic distances and angles relevant to the copper coordination spheres are listed in Table 4 (a full listing of bond lengths and bond angles is given in Table S4). The copper ions are separated by 3.296(2) Å with a Cu–O(H)–Cu bridge angle of 117.8(3)°. Two water molecules complete the square-pyramidal coordination with fairly long copper–oxygen separations (Cu1–O2 2.317(8), Cu2–O3 2.452(8) Å). A third water molecule (H25–O4–H26) appears to be hydrogen bonded to the axially coordinated waters via H18 and H23 (O2–O4 2.674(18) Å, O3–O4 2.743(20) Å, O2–H18–O4 177.4(15)°, O3–H23–O4 174.8(15)°) [54]. The two copper atoms are bound tightly within a framework of interconnecting five-membered chelate rings, which results in a somewhat distorted equatorial ligand plane (N2–Cu1–N4 77.4°, N2–Cu1–N1 80.6°, N1–Cu1–01 110.8°, O1–Cu1–N4 90.0°). The two copper centres are displaced slightly above the mean planes of the equatorial donor sets (Cu1 0.143 Å, Cu2 0.077 Å). Other structural analogues of this system include $[Ni_2(PHP)Cl(H_2O)_4]Cl_3 \cdot 2H_2O$ [31], $[Ni_2(PHP6Me)$-$Cl(H_2O)_4]Cl_3 \cdot 4.6H_2O$ [55] and $[Co_2(PHP6Me)Cl$-$(H_2O)_4Cl_3 \cdot 4.3H_2O$ [55]. These complexes involve an almost planar sexadentate ligand bound to two pseudo-octahedral metal centres bridged by a phthalazine (diazine) and a chlorine and with water molecules occupying the axial ligand positions. Much larger metal–metal separations are found (> 3.6 Å) resulting, in part, from longer contacts to the single atom chlorine bridge. Compounds V and VII are expected to have similar hydroxo-bridged structures to VI with the likelihood of axial water coordination

TABLE 3. Magnetic, electronic spectral and conductance data

	Compound	d–d (cm^{-1}) (ϵ(l mol^{-1} cm^{-1}))	μ_{eff} (r.t.) (μ_B)	$-2J$ (cm^{-1})	g^e	$\Lambda_m{}^a$ (mho mol^{-1} cm^2)
I	$[Cu_2(IMHP)(OH)(H_2O)_2](ClO_4)_3 \cdot CH_3OH$	[16700](12100), 17500(13300) 27800(18500)^a [15400], [19200], 22700^b	0.42	918 ± 14 74^c 0.11^d	2.076(6)	284
II	$[Cu_2(PHP)(OH)](ClO_4)_3 \cdot 0.25CH_3CH_2OH$	16700(28000), [18500](25500), [27800](37500), 30800(39500)^a [20000], [23800]^b	0.56	885 ± 57 60^c 0.035^d	2.119(9)	278
III	$[Cu_2(PHP\text{–}H)(OH)(H_2O)_2](ClO_4)_2$	16400(15800), [18200](12600), [27000](20000), 29400(23300)^a 19600^b	0.31	1017 ± 3 20^c 0.0011^d	2.123(6)	194
IV	$[Cu_2(PHP6Me\text{–}H)(OH)](ClO_4)_2 \cdot 0.5H_2O$	16400(15600), [18200](21000), 27000(22200), 30300(24700)^a [17500], 18900^b	0.29	1116 ± 15 50^c 0.0040^d	2.134(7)	187
V	$[Cu_2(APHP)(OH)](ClO_4)_3$	16400(17200), 29900(24700)^a [16000], [20000]^b	0.37	962 ± 4 21^c 0.033^d	2.165(5)	232
VI	$[Cu_2(APHP\text{–}H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$	16400(18400), 29900(25400)^a [15900], 20000, 28600^b	0.34	988 ± 6 60^c 0.00125^d	2.11(2)	169
VII	$[Cu_2(APHP\text{–}2H)(OH)(H_2O)_2](ClO_4) \cdot 2H_2O$	16400(16100), 29400(21600)^a 16000, 19800^b	0.22	1211 ± 14 40^c 0.0010^d	2.19(2)	90.3
VIII	$[Cu_2(APHP\text{–}H)(pyz)](ClO_4)_2$	16700(21700), 29400(23200)^a [16400], 18900^b	0.91	521 ± 3 80^c 0.0020^d	2.02(1)	170

[a] DMF solution. [b] Mull transmittance; [] = shoulder. [c] $N\alpha \times 10^6$ cgsu. [d] ρ. [e] e.s.d. in last digit given in parentheses.

TABLE 4. Interatomic distances (Å) and angles (°) relevant to the copper coordination spheres in $[Cu_2(APHP\text{-}H)(OH)(H_2O)_2](ClO_4)_2\cdot H_2O$ (**VI**)

Cu(1)–O(1)	1.900(6)	Cu(2)–O(3)	2.452(8)
Cu(1)–O(2)	2.317(8)	Cu(2)–N(5)	1.897(8)
Cu(1)–N(1)	2.030(8)	Cu(2)–N(7)	1.982(8)
Cu(1)–N(2)	1.956(8)	Cu(2)–N(8)	1.959(8)
Cu(1)–N(4)	1.985(8)	Cu(1)–Cu(2)	3.296(2)
Cu(2)–O(1)	1.949(6)		
Cu(1)–O(1)–Cu(2)	117.8(3)	O(1)–Cu(2)–N(5)	88.9(3)
O(1)–Cu(1)–N(1)	110.8(3)	O(1)–Cu(2)–N(7)	166.5(3)
O(1)–Cu(1)–N(2)	165.7(3)	O(1)–Cu(2)–N(8)	111.7(3)
O(1)–Cu(1)–N(4)	90.0(3)	N(5)–Cu(2)–N(7)	78.2(3)
N(1)–Cu(1)–N(2)	80.6(3)	N(5)–Cu(2)–N(8)	158.8(3)
N(1)–Cu(1)–N(4)	156.7(3)	N(7)–Cu(2)–N(8)	80.8(3)
N(2)–Cu(1)–N(4)	77.4(3)	O(1)–Cu(2)–O(3)	88.0(4)
O(1)–Cu(1)–O(2)	95.0(3)	O(3)–Cu(2)–N(5)	98.9(4)
O(2)–Cu(1)–N(1)	89.6(3)	O(3)–Cu(2)–N(7)	98.0(4)
O(2)–Cu(1)–N(2)	93.7(3)	O(3)–Cu(2)–N(8)	87.5(4)
O(2)–Cu(1)–N(4)	99.1(3)		

in **VII** but not in **V**. The binuclear centre dimensions are likely to be comparable in all three compounds.

The stoichiometry of complex **VI** indicates that the ligand exists as a monoanionic entity. Proton loss would be expected to occur at one of the exocyclic nitrogen sites (N3 or N6). A hydrogen atom (H8) was located on N3 from a difference map, while no hydrogen was located on N6. Examination of the bond lengths in the framework Cu2–N5–C15–N6 corroborates this finding but also indicates that charge delocalization has occurred from N6 into the phthalazine ring. The bond N4–C8 has substantial double bond character and the bond length 1.299(12) Å is comparable with equivalent bond lengths found in related hydroxo-bridged binuclear, square-pyramidal, phthalazine and pyridazine complexes which have neutral ligands [49]. The N5–C15 bond is significantly longer indicating enhanced single bond character. The N6–C15 bond length is significantly shorter than the corresponding bond length (C8–N3) on the neutral half of the molecule indicating some double bond character. Finally, in keeping with this situation, the Cu2–N5 bond length is significantly shorter than Cu1–N4 and copper–nitrogen (diazine) bond lengths found in the related pyridazine and phthalazine complexes, clearly indicating a build up of charge on nitrogen N5 [49]. It is also relevant to note that the angles Cu1–N4–N5(117.1(6)°) and Cu2–N5–N4(124.1(6)°) are significantly different, again denoting a difference involving bonding of the copper atoms to nitrogens N4 and N5.

The similarity between the ligands APHP, IMHP, PHP and PHP6Me (Fig. 1) would suggest that the same basic planar ligand environment of three nitrogen donors per copper would result in similar binuclear hydroxo-bridged structures for the other complexes to that found in **VI**. As in the case of the APHP complexes infrared data indicate that the perchlorate groups are ionic in all cases and so for **II** and **IV** square-planar copper chromophores seem likely while for **I** and **III** the possibility of weak coordination of axial water molecules to form a square-pyramidal derivative should be considered. The pyrazole derivative (**VIII**) is considered to have a square-planar structure involving a pyrazolide (N_2) bridge between the two copper centres, in addition to the phthalazine bridge.

Room temperature effective magnetic moments for all the compounds are very low, with the values for compounds **I**–**VII** (<0.6 BM) signalling very strong exchange between the copper(II) centres. Magnetic susceptibility measurements were performed on powdered samples of **I**–**V**, **VI**[*], **VII** and **VIII** in the temperature range 5–300 K and the results are summarized in Table 3. The best fit lines were calculated from the modified Van Vleck equation [56] for exchange coupled pairs of copper(II) ions (eqn. (1)).

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

In this expression $2J$ (in the spin Hamiltonian $\mathcal{H} = -2J\hat{s}_1\cdot\hat{s}_2$) 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 values of g and $-2J$ giving the best fit were obtained using a two variable non-linear regression analysis [57] with ρ and $N\alpha$, the temperature independent paramagnetism, as floating parameters. Diamagnetic susceptibility contributions were calculated in the normal way for the ligands and the metal centres [58]. Experimental variable temperature magnetic susceptibility data plots, including the best fit theoretical lines, are given for compounds **I**, **IV** and **VIII** in Figs. 3–5, respectively. See also 'Supplementary material'.

Exchange integrals ($-2J$) for all of the hydroxo-bridged compounds are very large (>880 cm^{-1}) indicating almost complete population of the spin-singlet magnetic ground state, even at room temperature. Good curve fits were obtained in all cases except for compound **II**, where, even though a poor fit was obtained, very strong exchange is still apparent. Spin exchange of this magnitude is a common feature

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[*] Variable temperature magnetic data obtained using an SHE Squid magnetometer, courtesy Dr C. A. Reed, University of Southern California.

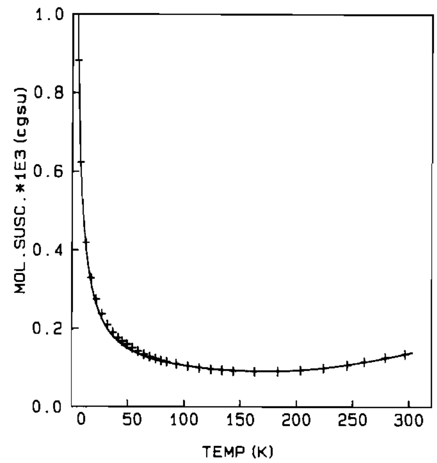

Fig. 3. Magnetic susceptibility data for $[Cu_2(IMHP)(OH)(H_2O)_2](ClO_4)_3 \cdot CH_3OH$ (I). The solid line was calculated from eqn. (1) with $g = 2.076(6)$, $-2J = 918(14)$ cm^{-1}, and $N\alpha = 74 \times 10^{-6}$ cgsu (cm^3 mol^{-1})/Cu and including 1.1% paramagnetic impurity ($\rho = 0.011$).

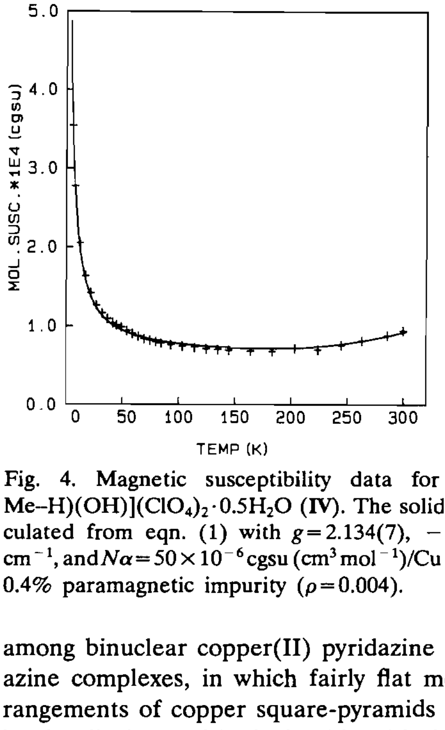

Fig. 4. Magnetic susceptibility data for $[Cu_2(PHP6\text{-}Me\text{-}H)(OH)](ClO_4)_2 \cdot 0.5H_2O$ (IV). The solid line was calculated from eqn. (1) with $g = 2.134(7)$, $-2J = 1116(15)$ cm^{-1}, and $N\alpha = 50 \times 10^{-6}$ cgsu (cm^3 mol^{-1})/Cu and including 0.4% paramagnetic impurity ($\rho = 0.004$).

among binuclear copper(II) pyridazine and phthalazine complexes, in which fairly flat molecular arrangements of copper square-pyramids are bridged by the diazine and by hydroxide with Cu–O(H)–Cu bridge angles in excess of 116° [49]. The total exchange situation for complexes of this sort can be considered to be the sum of contributions from the diazine (N–N) bridge and the hydroxide bridge, which are both aligned favourably with respect to an effective magnetic overlap with the $d_{x^2-y^2}$ copper magnetic orbital, at least in those cases that have been structurally documented [17, 18, 21, 44, 49]. Although the structure of only one compound in the present study (VI) has been determined, it is reasonable to assume that the other hydroxo-bridged species have

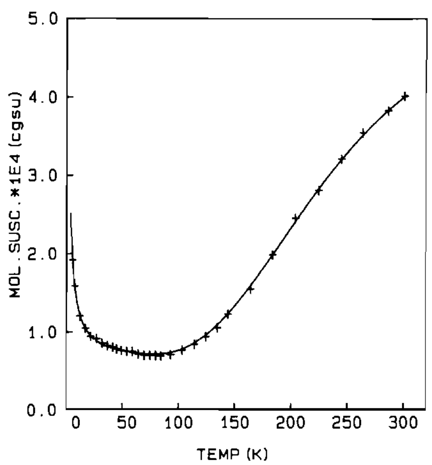

Fig. 5. Magnetic susceptibility data for $[Cu_2(APHP\text{-}H)(pyz)](ClO_4)_2$ (VIII). The solid line was calculated from eqn. (1) with $g = 2.02(1)$, $-2J = 521(3)$ cm^{-1} and $N\alpha = 80 \times 10^{-6}$ cgsu (cm^3 mol^{-1})/Cu and including 0.2% paramagnetic impurity ($\rho = 0.002$).

similar structures involving either square-planar or square-pyramidal copper(II) centres, for which a $d_{x^2-y^2}$ copper magnetic orbital ground state would be appropriate. A detailed comparison of these compounds, in terms of their differing exchange integrals cannot be made in the absence of structural parameters, but in the case of the related series of compounds V–VII some comment can be made on the basis of the charged state of the ligand.

The negative charge associated with the anionic nature of the ligand in VI is delocalized to some extent onto the phthalazine ring and to nitrogen N5. Such a tautomeric effect is reasonable, especially for neutral amino- and hydrazino-phthalazine ligands [27]. A build up of charge on a ligand donor site would reasonably be expected to affect the exchange situation by increasing electron delocalization within the copper magnetic orbital and therefore lead to enhanced exchange in comparison with a neutral ligand species. Such an effect has been observed in a series of bis-bidentate bridged dicopper(II) complexes involving oxalate, oxamide and dithio-oxamide ligand bridges with antiferromagnetic exchange increasing significantly as the electronegativity of the bridging ligand atom decreased [59]. Exchange for the APHP series of compounds follows the order V < VI < VII, with the largest exchange occurring for VII, which involves a doubly deprotonated ligand. Within the constraints of the previous argument these results are reasonable. The major factor affecting exchange in hydroxo-bridged compounds of this sort is the angle at the hydroxide bridge, and this feature has been assessed for both mono- [49] and di-hydroxo-bridged binuclear copper systems [60] with $d_{x^2-y^2}$ or d_{xy} ground states with exchange increasing as a function of increasing oxygen bridge angle in a linear fashion. For compounds **V**, **VI** and **VII** it is reasonable to assume that as the number of deprotonated ligand sites increases the size of the five-membered ring, which constitutes the binuclear centre, would decrease, probably resulting in a successive decrease in hydroxide bridge angle. This effect would not lead to increased exchange, as is observed, thus supporting the previous argument.

The dramatic decrease in exchange integral for the pyrazole derivative **VIII** (Fig. 5) is a clear indication that the hydroxide bridge has been displaced and has been replaced by pyrazolide. Molecular models indicate that such a bridge would fit reasonably between the copper(II) centres in a planar arrangement and such a displacement is in keeping with other binuclear copper(II) systems in which hydroxo-bridged species have been reacted with pyrazole [61]. The lack of information on dicopper(II) complexes involving just pyrazole bridges makes it difficult to estimate the contribution of the pyrazolide bridge to total exchange in this system. A recent report on the structural and magnetic properties of the complex ion $[(H_2B(pz)_2)_2Cu_2(pz)_2Cl]^-$ (pz = pyrazolide), which involves two square-pyramidal copper(II) centres bridged axially by chlorine and with a *cis*-equatorial bridging arrangement of two canted pyrazolides, has net antiferromagnetic exchange with $-2J \approx 240$ cm^{-1} [62]. A related system involving just two canted pyrazolide groups bridging two square-planar copper(II) centres, in which the copper square planes have an interplanar angle of 85.1°, has comparable antiferromagnetic exchange with $-2J = 270$ cm^{-1} [63]. Structurally these complexes are quite different from **VIII**, which is expected to have a planar arrangement of donors about the binuclear centre, and so projections based on these magnetic data may not be realistic.

Studies on related binuclear copper(II) complexes involving tetradentate (N_4) phthalazine and pyridazine ligands show that in general pyridazine bridged complexes exhibit stronger antiferromagnetic exchange than those with phthalazine bridges [49, 64]. The complexes $Cu_2(PTP)Cl_4$ (PTP = 3,6-bis(2-pyridylthio)pyridazine) [64] and $Cu_2(PAP46Me)Cl_4$ (PAP46Me = 1,4-di(4,6-dimethyl-2-pyridylamino)-phthalazine) both have very similar diazine bridged binuclear structures involving square-pyramidal copper centres, but with an asymmetric dichloro bridge, in which the two bridging chlorine atoms act as both equatorial and axial bridges to both copper centres. This orthogonal arrangement of halogen bridges would result in a situation where the antiferromagnetic exchange component would be dominated by the diazine bridge. In the absence of significant ferromagnetic coupling via the chlorine bridges, which would seem reasonable, the stronger antiferromagnetic exchange for $Cu_2(PTP)Cl_4$ ($-2J = 130.5$ cm^{-1}; $Cu_2(PAP46Me)Cl_4$, $-2J = 55.2$ cm^{-1}) can be attributed to an effectively shorter exchange pathway associated with the pyridazine bridge. For a phthalazine bridge the fused benzene ring provides an extended delocalization pathway in addition to the pyridazine ring, which would effectively reduce antiferromagnetic coupling.

Halogens acting both as bridging and terminal ligands have been shown to exert an electron withdrawing effect on electron density in the copper magnetic orbital manifold and that antiferromagnetic coupling diminishes as I > Br > Cl, in keeping with electronegativities [49, 64, 65]. A comparison of the isostructural pair of compounds $Cu_2(PTP)Cl_4$ and $Cu_2(PTP)Br_4$ ($-2J = 243.5$ cm^{-1}) illustrates the importance of this effect. A comparison of these two compounds with the symmetrically chloro-bridged derivative $[Cu_2(PTP)_2Cl](ClO_4)_3 \cdot CH_3CN$ ($-2J = 480$ cm^{-1}) [66], which involves in plane bridging of the square-pyramidal copper(II) centres by two pyridazines, indicates that pyridazine causes moderately

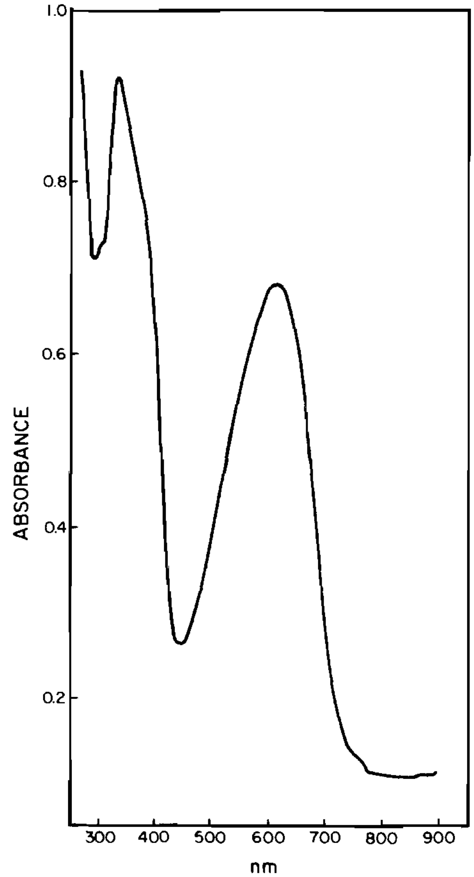

Fig. 6. Electronic spectrum of $[Cu_2(APHP-H)(OH)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (VI) in DMF solution.

strong antiferromagnetic coupling with an estimated contribution of about $-240\ cm^{-1}$ and that the bromine ligands may not contribute significantly to the overall exchange picture. Relating the exchange effects in $Cu_2(PTP)Cl_4$ and $Cu_2(PTP)Br_4$ with $Cu_2(PAP46Me)Cl_4$ suggests that the phthalazine bridge could make a contribution of around $-100\ cm^{-1}$. Although the angles Cu1–N4–N5 (117.1°) and Cu2–N5–N4 (124.1°) in **VI** are slightly different from comparable angles in the PTP and PAP46Me complexes the contribution of the phthalazine bridge to total exchange is likely to be similar. These results indicate that in the pyrazole bridged complex **VIII** the exchange is dominated by pyrazole itself and that in the other, hydroxo-bridged derivatives the hydroxide bridge is the major pathway for antiferromagnetic exchange. The likely planar arrangement of the pyrazolide group would certainly be consistent with its role in dominating exchange in **VIII**.

The molecular pathways for exchange in these multiply-bridged complexes can be likened to an arrangement of parallel electronic circuits connecting the two 'electron rich' metal centres, which attempt to communicate electronically via this circuitry. The extent to which this communication takes place will depend on such factors as distance through which exchange occurs, the angle subtended by an exchange bridge, geometrical orientation of communicating orbitals, the number of bridges etc., and the partitioning of exchange can be examined by a selective comparison of carefully chosen compounds with appropriate features. However, this approach must involve a more comprehensive examination of related compounds than presented here and can be contrasted with the simpler approach to an understanding of the structural features that affect exchange in the dihydroxo-bridged binuclear copper(II) complexes described in the classic study by Hatfield and coworkers [60].

The solid state, mull transmittance, electronic spectra of the complexes are generally dominated by intense, low energy, absorptions at energies greater than 15 000 cm^{-1}, associated with charge transfer transitions. The ligands themselves are characterized by having one very intense band in the range 24 000–25 000 cm^{-1} and another above 30 000 cm^{-1} in solution in DMF and no absorption below 20 000 cm^{-1}. In contrast all the complexes exhibit very intense visible absorption in DMF in the range 16 400–17 400 cm^{-1} with higher energy, intense absorption in excess of 27 000 cm^{-1} (Table 3) (see Fig. 6 for a typical spectrum). The observation of such intense visible bands in this energy range is most unusual and poses the question as to the electronic origin of the transitions involved.

The ease with which the ligands lose protons under mildly basic conditions allows a series of complexes involving neutral, mono-anionic and di-anionic ligand to be synthesized (Table 3). For complexes **V**, **VI** and **VII** the charged state of the ligand itself appears to have little effect on the energy or intensity of the charge transfer transitions either in the visible or the ultraviolet regions. Nitrogen heterocyclic donor ligands e.g. pyridine, 2,2′-bipyridine, *o*-phenanthroline, generate complexes with readily oxidizable transition metal centres, which exhibit fairly low energy metal-to-ligand charge transfer transitions occurring at lower energies than typical π–π^* transitions associated with the ligands themselves [67]. The ligands under discussion contain typical donor groups that would favour low energy charge transfer transitions of this sort, and these bands are tentatively assigned to copper to ligand charge transfer transitions. The higher energy charge transfer absorptions are assigned as π–π^* intraligand transitions. The high intensity of the visible bands obscured any other bands which could be assigned to d–d transitions.

Supplementary material

Anisotropic thermal parameters, positional parameters for the hydrogen atoms, angles and distances pertaining to the ligand and perchlorate groups, calculated and observed structures factors and variable temperature magnetic suspectibility plots for **III**, **V**, **VI** and **VII** are available from the authors.

Acknowledgment

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