Copper Co-ordination Chemistry of some Quadridentate Pyridazine and Phthalazine (N_4) Thioether Ligands. Binuclear Copper(II) Complexes exhibiting Two-electron Reduction at Positive Potentials†

Tai Chin Woon, Robert McDonald, Sanat K. Mandal, Laurence K. Thompson,* and Sean P. Connors
Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7
Anthony W. Addison
Department of Chemistry, Drexel University, Philadelphia, Penn. 19104, U.S.A.

Binuclear, hydroxo-bridged, copper(II) complexes of a series of quadridentate pyridazine and phthalazine thioether ligands involving nitrogen donor groups (derived from pyridine, imidazole, benzimidazole) exhibit room-temperature magnetic moments in the range 1.1—1.7 B.M., indicative of antiferromagnetically coupled binuclear copper(II) centres. Cyclic voltammetry and coulometry on most of these systems indicate reversible or quasi-reversible redox processes, involving two-electron transfer, at positive potentials (0.23—0.49 V *vs.* a saturated calomel electrode in CH_3CN or dimethylformamide). Mononuclear copper(II) derivatives, involving bidentate ligands, also exhibit reduction at positive potentials. Catecholase activity involving 3,5-di-t-butylbenzene-1,2-diol has been demonstrated for the hydroxo-bridged complex $[Cu_2(ptpd)(OH)Cl_3]\cdot EtOH$ [ptpd = 3,6-di(2'-pyridylthio)pyridazine], in which a Michaelis-Menten kinetic treatment gave $K_M = 3.4 \times 10^{-4}$ mol dm^{-3} and a value of $k_p = 2.1 \times 10^{-2}$ s^{-1} for the dissociation of the catechol–complex intermediate.

Quadridentate phthalazine[1-18] and pyridazine ligands[2-4,19-24] involving nitrogen donor centres have been shown to generate principally binuclear transition metal complexes. For the most part the binuclear copper(II) complexes involve a hydroxide bridge, in addition to the diazine bridge, a characteristic feature associated with the strong antiferromagnetic coupling observed for these systems. Exchange integrals ($-2J$) have been observed in the range 200—800 cm^{-1} and the magnitude of the exchange has been shown to be a function of the hydroxo-bridge angle and the copper ion ground state.[5,13,15,16,19] Electrochemical studies on a number of these systems have shown two-electron reduction at positive potentials, an unusual feature associated with synthetic binuclear complexes, but a characteristic feature of certain binuclear copper–protein centres (fungal laccase, $E_{\frac{1}{2}}$ +782 mV;[25] tree laccase, $E_{\frac{1}{2}}$ +434 mV;[25] tyrosinase, $E_{\frac{1}{2}}$ +360 mV[26] *vs.* standard hydrogen electrode). For the complex $[Cu_2(6\text{-mpaph})(OH)Cl_3]\cdot 3H_2O$ [6-mpaph = 1,4-di(6'-methyl-2'-pyridylamino)phthalazine], which involves a hydroxo-bridged, antiferromagnetically coupled binuclear centre ($-2J$ = 432 cm^{-1}), an almost reversible, two-electron redox process is observed at $E_{\frac{1}{2}}$ +0.44 V [*vs.* a saturated calomel electrode (s.c.e.) at a platinum electrode with 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ in dimethylformamide (dmf)].[27] For the complex $[Cu_2(dmppd)(OH)Cl_2][CuCl_3(H_2O)]\cdot H_2O$ [dmppd = 3,6-bis(3',5'-dimethyl-1'-pyrazolyl)pyridazine], which has an essentially diamagnetic hydroxo-bridged binuclear cation, a quasi-reversible two-electron redox process is observed at $E_{\frac{1}{2}}$ +0.42 V (*vs.* s.c.e.) under the same conditions.[27] The fact that complexes of this sort have large Cu–O–Cu angles (112—126°), antiferromagnetically coupled binuclear copper(II) centres, and positive reduction potentials makes them particularly attractive as models for the active sites in binuclear copper proteins.[28]

In the present study we describe copper complexes of a series of quadridentate (N_4) ligands based on pyridazine and phthalazine as the binucleating fragments, in which the peripheral nitrogen donor groups are bound to the diazine centres by a thioether linkage (Figure 1). Binuclear hydroxo-bridged derivatives of ptpd [3,6-di(2'-pyridylthio)pyridazine], ptph [1,4-di(2'-pyridylthio)phthalazine], bitpd [3,6-di(2'-benzimidazolylthio)pyridazine], and mimtpd [3,6-di(1'-methyl-2'-imidazolylthio)pyridazine] and mononuclear complexes of both ptpd and mimtpd are described. Reduced room-temperature magnetic moments are observed for all hydroxo-bridged derivatives, indicative of exchange coupling between the copper centres, and in all cases studied positive reduction potentials (>0.23 V *vs.* s.c.e.) are observed for the binuclear copper complexes.

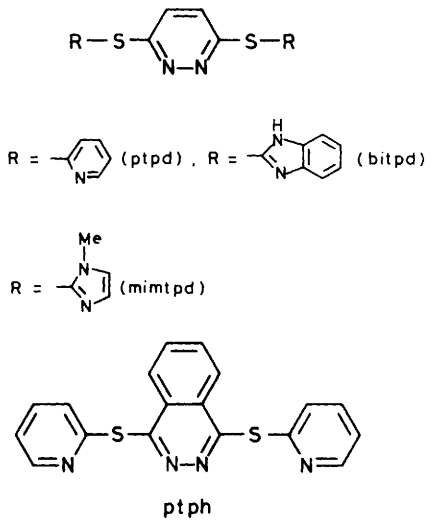

Figure 1. Structural formulae of the ligands ptpd, bitpd, mimtpd, and ptph

† *Non-S.I. unit employed:* B.M. = 9.274 × 10^{-24} J T^{-1}.

Preliminary details of the structure of the mononuclear complex $[Cu(ptpd)_2(H_2O)][ClO_4]_2 \cdot 3H_2O$, which has a very positive redox potential ($E_{\frac{1}{2}} = 0.57$ V *vs.* s.c.e.). are also reported.

Experimental

Synthesis of Ligands.—Unless otherwise stated, reagents were those available commercially and were used without further purification.

3,6-*Di*(2′-*pyridylthio*)*pyridazine* (*ptpd*). 3,6-Dichloropyridazine (5.2 g, 0.035 mol) and pyridine-2-thiol (7.8 g, 0.070 mol) were reacted together in absolute ethanol (60 cm^3) under reflux for 30 min with the formation of a red solution which was then adjusted to pH 9 with 5 mol dm^{-3} aqueous sodium hydroxide. The solvent was flash-evaporated and the black residue extracted into $CHCl_3$–charcoal. The chloroform solution was filtered and the solvent removed under vacuum and the resulting solid extracted into toluene–hexane. On cooling a light brown powdery solid formed. Yield 6.6 g (63%); m.p. 134—137 °C (Found: C, 56.4; H, 3.55; N, 18.7. Calc. for $C_{14}H_{10}N_4S_2$: C, 56.4; H, 3.40; N, 18.9%). Mass spectrum: *m/z* 298 (M^+, 15%), 192 (14), 188 (100), 160 (33), 148 (10), 135 (13), 110 (33), and 78 (80). ^1H N.m.r. data in $CDCl_3$ are consistent with the structure of ptpd.

3,6-*Di*(2′-*benzimidazolylthio*)*pyridazine* (*bitpd*). 3,6-Dichloropyridazine (5.2 g, 0.035 mol) and benzimidazole-2-thiol (10.5 g, 0.070 mol) were each dissolved in ethanol (100 cm^3) and the solutions mixed. After refluxing for 10 min a white precipitate formed. Refluxing was continued for 2 h and the mixture brought to pH 9 with aqueous NaOH. The white solid was filtered off, washed with water and ethanol, dried under vacuum, and recrystallized from methanol. Yield 13 g (100%); m.p. 273—275 °C (Found: C, 57.4; H, 3.30; N, 22.4. Calc. for $C_{18}H_{12}N_6S_2$: C, 57.4; H, 3.20; N, 22.3%). Mass spectrum: *m/z* 376 (M^+, 8%), 227 (60), 199 (5), 175 (7), 150 (100), 122 (23), 118 (15), 90 (17), and 78 (16). δ_H {80 MHz, [$^2H_6$]dimethyl sulphoxide (dmso), standard $SiMe_4$} 7.13 (4 H, m, benzimidazole H_α), 7.43 (4 H, m, benzimidazole H_β), 7.52 (2 H, s, pyridazine).

3,6-*Di*(1′-*methyl*-2′-*imidazolylthio*)*pyridazine* (*mimtpd*). Solutions of 3,6-dichloropyridazine (7.5 g, 0.050 mol) and 1-methylimidazole-2-thiol (11.4 g, 0.100 mol), each in methanol (30 cm^3), were combined and the mixture refluxed for 20 min. The reaction mixture was cooled and adjusted to pH 9 with 4 mol dm^{-3} aqueous NaOH and the solvent removed *in vacuo* until a white solid formed. The product was filtered off, washed with water, and recrystallized from acetonitrile (charcoal) to give colourless prisms and dried *in vacuo* at 65 °C. Yield 8 g (52%), m.p. 146—148 °C (Found: C, 47.4; H, 3.95; N, 27.6. Calc. for $C_{12}H_{12}N_6S_2$: C, 47.4; H, 3.95; N, 27.6%). Mass spectrum: *m/z* 304 (M^+, 7%), 191 (100), 145 (8), 114 (49), 113 (45), 96 (79), 72 (98), and 55 (22).

1,4-*Di*-(2′-*pyridylthio*)*phthalazine* (*ptph*). Pyridine-2-thiol (2.2 g, 0.020 mol) was dissolved in dichloroethane (100 ml) and added dropwise to a stirred solution of 1,4-dichlorophthalazine[29] (1.99 g, 0.010 mol) in dichloroethane (50 cm^3). The creamy precipitate was filtered after 30 min, washed with ethanol, and air dried. It was then dissolved in water, neutralized with Na_2CO_3, and extracted into chloroform (350 cm^3). The chloroform solution was dried over $MgSO_4$ and the volume reduced to 20 cm^3. On standing yellow crystals formed which were filtered off and dried in air. Yield 2.3 g (67%); m.p. 205—206 °C (Found: C, 61.4; H, 3.55; N, 15.9. Calc. for $C_{18}H_{12}N_4S_2$: C, 61.3; H, 3.55; N, 15.9%). Mass spectrum: *m/z* 348 (M^+, 10%), 238 (100), 187 (24), 128 (97), 111 (50), 101 (24), 83 (16), 78 (73), and 67 (71).

$[Cu_2(ptpd)(OH)Cl_3] \cdot EtOH$ (**1**).—$CuCl_2 \cdot 2H_2O$ (1.5 g, 0.0088 mol) was dissolved in water (25 cm^3) and a solution of ptpd (0.40 g, 0.0013 mol) in ethanol (20 cm^3) added and the mixture heated on a steam-bath until green crystals formed. After cooling the product was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo*. Compounds (**2**), (**3**), and (**4**) (H_2O and MeOH used as solvents) were prepared in a similar manner.

$[Cu_2(mimtpd)Cl_4] \cdot 3.5H_2O$ (**5**).—The ligand mimtpd (0.50 g, 0.0016 mol) was dissolved in acetonitrile (25 cm^3) and added to a solution of $CuCl_2 \cdot 2H_2O$ (0.70 g, 0.0041 mol) in water (10 cm^3) and the mixture warmed on a steam-bath. On cooling and addition of diethyl ether a green precipitate formed which was filtered off, washed with ether, and dried *in vacuo*. Compounds (**6**)—(**8**) were prepared in a similar manner using methanol as solvent.

$[Cu_2(ptph)(OH)Cl_3] \cdot MeOH \cdot H_2O$ (**9**).—The ligand ptph (0.35 g, 0.001 mol) was dissolved in methanol (50 cm^3) and a solution of $CuCl_2 \cdot 2H_2O$ (0.35 g, 0.002 mol) in water (5 cm^3) added. The green solution was heated on a steam-bath for 30 min and allowed to evaporate slowly over 2—3 d. Green crystals formed which were filtered off, washed with methanol, and dried *in vacuo*. Compound (**10**) was prepared in a similar manner using dmf–H_2O as the solvent system.

Analyses.—Carbon, H, and N analyses were carried out by Canadian Microanalytical Service, Vancouver. Copper analyses were determined by atomic absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO_3, or *aqua regia*. Elemental analyses are quoted in Table 1.

Physical Measurements.—Electronic spectra were recorded with a Cary 17 spectrometer and i.r. with a Perkin-Elmer 283 spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn 7600 Faraday magnetic susceptibility system coupled to a Cahn gram electrobalance. Nuclear magnetic resonance spectra were run as solutions in deuteriochloroform or [$^2H_6$]dmso using a Bruker WP80 spectrometer ($SiMe_4$ internal standard) and mass spectra were obtained using a V.G. Micromass 7070 HS spectrometer with a direct insertion probe.

All electrochemical measurements were carried out under a nitrogen atmosphere at room temperature in CH_3CN or dmf, with 0.1 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte, using a BAS CV27 Voltammograph and a Houston 2000 Omnigraph *X*–*Y* recorder. Three electrode measurements (cyclic voltammetry) were carried out using platinum or glassy-carbon working electrodes, a platinum auxiliary electrode, and a saturated calomel reference electrode. Constant-potential electrolysis was performed with a platinum mesh 'flag' working electrode, a platinum mesh auxiliary electrode, and s.c.e. reference using the CV27 coulometer. Dilute solutions [(2—3) × 10^{-4} mol dm^{-3}] of the complexes were used and potentials are compared with the ferrocene–ferrocenium couple. Potentials quoted are uncorrected for junction potentials.

Results and Discussion

Spectroscopy, Magnetism, and Structure.—The diazine moiety in quadridentate 1,4-disubstituted phthalazines and 3,6-disubstituted pyridazines has been shown to be an effective binucleating centre, bringing the metal ions in binuclear derivatives into close proximity[1-24,27] with the formation of hydroxo-bridged complexes in most cases involving copper. Ligands of this sort have been synthesized by nucleophilic displacement from halogenated pyridazines and phthalazines and by ring expansion of disubstituted isoindolines. In all

Table 1. Analytical data (%)

Compound	Colour	Found C	Found H	Found N	Found Cu	Calc. C	Calc. H	Calc. N	Calc. Cu
(1) $[Cu_2(ptpd)(OH)Cl_3]\cdot EtOH$	Green	31.1	2.65	9.15	20.6	31.3	2.80	9.15	21.4
(2) $[Cu_2(ptpd)(OH)Br_3]\cdot 0.5H_2O$	Green	24.4	1.60	8.05	17.9	24.3	1.75	8.10	18.4
(3) $[Cu_2(ptpd)(OH)(NO_3)_3]$	Blue	26.9	1.85	15.3	19.3	26.8	1.75	15.6	20.2
(4) $[Cu(ptpd)_2(H_2O)][ClO_4]_2\cdot 3H_2O$	Blue	35.9	2.85	11.8		36.1	3.00	12.0	
(5) $[Cu_2(mimtpd)Cl_4]\cdot 3.5H_2O$	Green	22.7	2.40	13.2	20.2	22.6	3.00	13.2	20.0
(6) $[Cu_2(mimtpd)_2(OH)][ClO_4]_3\cdot H_2O$	Blue	27.0	2.75	15.7	11.0	27.0	2.55	15.7	11.9
(7) $[Cu(mimtpd)Br_2]\cdot 2.5H_2O$	Blue	25.0	2.75	14.5	11.2	25.2	3.30	14.7	11.1
(8) $[Cu(mimtpd)(NO_3)_2]\cdot 4H_2O$	Blue	25.4	2.45	20.7	11.7	25.5	3.55	19.9	11.3
(9) $[Cu_2(ptph)(OH)Cl_3]\cdot MeOH\cdot H_2O$	Green	35.1	2.50	8.60	19.8	35.2	2.95	8.65	19.6
(10) $[Cu_2(bitpd)(OH)Cl_3]\cdot dmf\cdot 0.5H_2O$	Green	35.4	2.95	13.8	17.3	35.6	2.95	13.8	17.9

Table 2. Spectral and magnetic data

Compound	I.r. (ν/cm^{-1})	*d–d* (ν/cm^{-1})[a]	$\mu_{eff.}$[b]	Λ_M/Ω^{-1} cm^2 mol^{-1}
(1)	3 500 (OH); 1 020;[c] 305, 280 (Cu–Cl)	14 900 [25 000] 14 300 (220)[d] 11 110 (168), 23 300 (600)[e]	1.62	21 (CH_3CN) 31 (dmf)
(2)	3 500 (OH); 1 022;[c] 280, 250 (Cu–Br)	11 600, 14 900 [22 700] 11 400 (166), 15 400 (75)[e]	1.21	74 (dmf)
(3)	3 500 (OH); 1 755, 1 735, 1 723 ($\nu_1 + \nu_4$ NO_3^-); 1 015[c]	16 700 13 000 (90)[e]	1.05	250 (dmf)
(4)	3 580, 3 520 (H_2O); 1 090 (ClO_4^-)	16 900 17 200 (215)[d]	1.86	
(5)	3 400 (H_2O); 290, 270 (Cu–Cl)	11 100, 23 800	1.88	
(6)	3 550 (OH); 3 480, 3 400 (H_2O); 1 090 (ClO_4^-)	[12 050] 15 500	1.61	
(7)	3 450, 3 400 (H_2O)	[11 800] 13 200	1.81	
(8)	3 400 (H_2O); 1 746, 1 733, 1 714 ($\nu_1 + \nu_4$ NO_3^-)	[11 100] 15 000	2.01	
(9)	3 610 (OH); 3 500 (H_2O, MeOH); 1 020[c]	14 800 11 100 (184), 23 500 (570)[e]	1.66	45 (dmf)
(10)	3 560 (OH); 3 420 (H_2O); 1 655 (dmf)	11 200, 14 800	1.15	

[a] Mull transmittance spectra; shoulders are given in square brackets. [b] Room temperature. [c] Pyridine ring breathing mode indicative of pyridine co-ordination (ref. 5). [d] Solution spectrum in CH_3CN (ε/dm^3 mol^{-1} cm^{-1}). [e] Solution spectrum in dmf (ε/dm^3 mol^{-1} cm^{-1}).

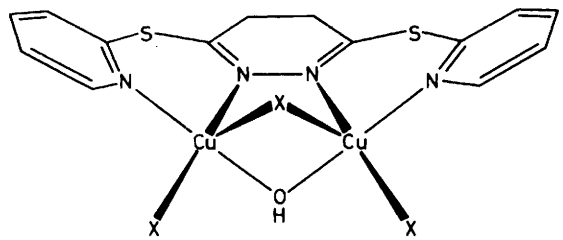

Figure 2. Structural representation of complexes (**1**) (X = Cl) and (**2**) (X = Br)

previously reported cases the ligands have involved nitrogen donor substituents (*e.g.* pyridines, imidazoles, pyrazoles) bound directly to the diazine moiety or *via* an intervening secondary amine centre. In this work the ligand syntheses are based on the very effective nucleophilic displacement of chlorine from 3,6-dichloropyridazine and 1,4-dichlorophthalazine by thiol derivatives. In all cases six-membered chelate rings are formed with thioether linkages between the peripheral nitrogen donors and the diazine rings.

The ligand ptpd resembles paph [1,4-di(2′-pyridylamino)phthalazine] and its derivatives[5–18,27] and forms hydroxo-bridged binuclear copper complexes with reduced room-temperature magnetic moments indicative of antiferromagnetic coupling between the metal centres. Solid-state electronic spectral and i.r. data for (**1**) and (**2**) (Table 2) are consistent with square-pyramidal metal centres in which a terminal and bridging halogen are assumed to be bound to each copper centre in addition to a hydroxide bridge (Figure 2). Structurally these systems should resemble the complexes $[Cu_2(paph)(OH)X_3]$ (X = Cl or Br), which have been shown to have five-co-ordinate, triply bridged binuclear centres[6,12] and have comparable electronic spectra. The nitrate complex, (**3**), has a higher energy visible absorption than (**1**) and (**2**) in the solid state which can be interpreted in terms of a square-pyramidal or perhaps distorted-octahedral stereochemistry involving co-ordinated nitrate. The very low room-temperature magnetic moment associated with this system suggests a fairly large Cu–O(H)–Cu bridge angle with the possibility of a nitrate group bridging the two metal centres also. The complex $[Cu_2(4\text{-mpaph})(OH)(H_2O)_2(NO_3)_2]NO_3$ [4-mpaph = 1,4-di(4′-methyl-2′-pyridylamino)phthalazine] has been shown to have a triply bridged binuclear centre involving a diazine, a hydroxide, and a nitrate bridge and a room-temperature magnetic moment of 1.02 B.M. ($-2J$ = 497 cm^{-1}).[16] Infrared data for (**3**) indicate three nitrate combination bands (Table 2)[30] which can be interpreted in terms of such a structural arrangement. Reaction of ptpd with copper perchlorate, even when present in excess, produces only the mononuclear derivative $[Cu(ptpd)_2(H_2O)][ClO_4]_2\cdot 3H_2O$ (**4**), involving two bidentate ligands each bound *via* a pyridine and pyridazine nitrogen and a co-ordinated water molecule in a five-co-

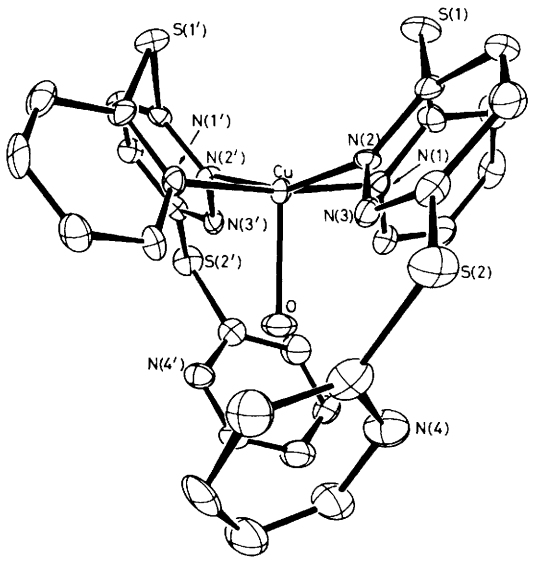

Figure 3. The structure of $[Cu(ptpd)_2(H_2O)]^{2+}$ (**4**): monoclinic, space group $C2/c$, $R = 0.032$; bond lengths, Cu–N(1) 2.016(8), Cu–N(2) 1.993(9), Cu–O 2.136(11) Å; bond angles, N(1)–Cu–N(1') 172.8(4), N(2)–Cu–N(2') 158.9(4), N(1)–Cu–N(2) 89.0(4), N(1)–Cu–N(2') 89.7(4)°

Table 3. Electrochemical data

Compound[a]	$E_{\frac{1}{2}}$/V *vs.* s.c.e.	ΔE_p/mV[b]	I_{pc}/I_{pa}[c]
(**1**)	0.49[d]	120 (r)	1.03
	0.47[e]	130 (qr)	
(**2**)	0.44[e]	180 (qr)	0.96
(**3**)	0.23[e]	290	0.98
(**9**)	0.47[d]	120 (r)	1.01
(**10**)	0.45[e]	110 (qr)	1.01
(**7**)	0.37[d]	150 (qr)	0.96
(**4**)	0.57[f]	200	1.02

[a] Concentrations (2—3) × 10^{-4} mol dm^{-3}. [b] Scan rate 200 mV s^{-1}; r = reversible, qr = quasi-reversible. [c] I_{pc} = Cathodic current, I_{pa} = anodic current. [d] Pt working electrode, CH_3CN solvent ($[NEt_4][ClO_4]$ electrolyte). [e] Glassy carbon working electrode, dmf solvent ($[NEt_4][ClO_4]$ electrolyte). [f] Glassy carbon working electrode, CH_3CN solvent ($[NEt_4][ClO_4]$ electrolyte).

ordinate, square-pyramidal structure (Figure 3).[31] The high-energy visible absorption exhibited by (**4**) is consistent with a five-co-ordinate derivative involving four in-plane nitrogen donor groups. The formation of mononuclear bis-ligand derivatives with anions which are weak donors has been observed with other related ligands, *e.g.* paph and 4-mpaph.[10]

The ligand mimtpd, which involves *N*-methylimidazole peripheral donor groups, also forms both binuclear and mononuclear derivatives. However, unlike ptpd, mononuclear derivatives are formed with copper bromide and copper nitrate. The tetrachloride complex (**5**), formed from aqueous solution, has a 'normal' magnetic moment at room temperature indicating the absence of antiferromagnetic coupling between the copper centres. Terminal copper–chlorine bonds are indicated by i.r. data and a possible structural arrangement for this complex involves two four-co-ordinate copper centres bridged by just the pyridazine group. The perchlorate complex (**6**) is clearly a hydroxo-bridged species and the reduced room-temperature magnetic moment suggests spin coupling between the copper centres. The presence of two ligands per binuclear

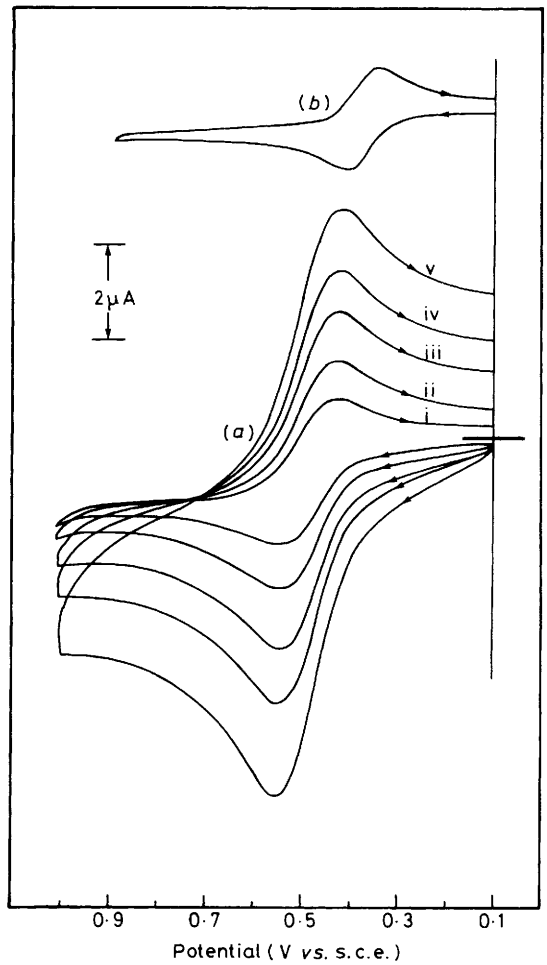

Figure 4. Cyclic voltammograms (*a*) for (**1**) (Pt electrode, CH_3CN solvent, $[NEt_4][ClO_4]$ electrolyte), at scan rates of (i) 50, (ii) 100, (iii) 200, (iv) 300, (v) 400 mV s^{-1}; (*b*) ferrocene–ferrocenium couple

centre is unusual but can be rationalised in terms of a structure in which the two ligands provide four in-plane nitrogen donors per metal and the hydroxide bridge acts as an axial, fifth ligand to each metal centre.

The two mononuclear derivatives (**7**) and (**8**) are formed despite the presence of an excess of metal salt during synthesis. Both complexes are likely to involve a bidentate ligand with one imidazole nitrogen and one pyridazine nitrogen binding to the metal centre. Co-ordinated water is suggested in both systems, with the probability of co-ordinated bromine in (**7**) and unidentate nitrate in (**8**). The electronic spectra can be interpreted, in both cases, in terms of square-pyramidal copper centres with the lower energy absorption in (**7**) indicating bromine co-ordination.

The phthalazine ligand ptph is likely to resemble paph in its co-ordination chemistry (paph involves an exocyclic NH in place of the thioether sulphur) and also to be closely related to ptpd. The chloro complex (**9**) is clearly very similar to (**1**) and is likely to involve a hydroxide bridge, co-ordinated chlorine (bridging and terminal), and a five-co-ordinate stereochemistry (Figure 2). For a related series of binuclear hydroxo-bridged pyridylphthalazine complexes involving $d_{x^2-y^2}$ ground states, it has been shown that a linear relationship holds between hydroxide bridge angle and exchange integral ($-2J$) and that a linear relationship exists between room-temperature magnetic moment and Cu–O(H)–Cu angle.[15] Since the room-temperature magnetic moment of (**9**) is very similar to that of (**1**)

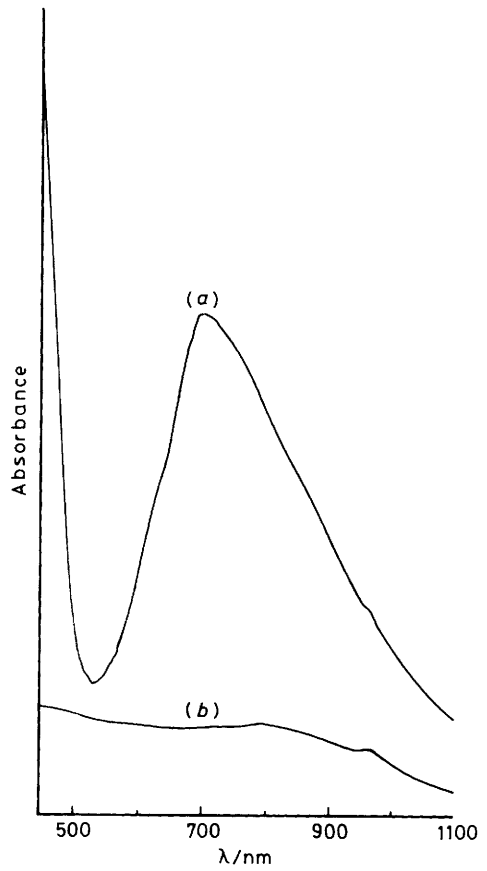

Figure 5. Electronic (*d–d*) spectra for (**1**) in CH_3CN (3×10^{-4} mol dm^{-3}, 0.1 mol dm^{-3} $[NEt_4][ClO_4]$), (*a*) before reduction; (*b*) after reduction

and also the complex $[Cu_2(paph)(OH)Cl_3]\cdot 1.5H_2O$, which has a five-co-ordinate hydroxo-bridged structure,[5,12] then antiferromagnetic exchange in these systems is likely to be comparable ($-2J \sim 200$ cm^{-1}) along with similar hydroxo-bridge angles. Complex (**10**) is clearly an analogous five-co-ordinate derivative but the very low magnetic moment for this system indicates the probability that the bridge angle at oxygen is much larger. It has been demonstrated that the introduction of a methyl substituent at the pyridine 6-position in paph causes a dramatic expansion of the binuclear centre. In the case of the complex $[Cu_2(paph)(OH)Cl_3]\cdot 1.5H_2O$ the Cu–O(H)–Cu bridge angle is *ca.* 100° while for $[Cu_2(6\text{-}mpaph)(OH)Cl_3]\cdot 3H_2O$ a corresponding angle of 112.2° is observed,[27] with a proportionate increase in the copper–copper separation. The ligand bitpd, with bulky peripheral benzimidazole groups, can be considered to provide a similar steric perturbation possibly resulting in an expanded binuclear centre and consequently a much lower room-temperature magnetic moment.

Conductance data (Table 2) indicate that in acetonitrile and dmf (**1**) is essentially undissociated but (**2**) appears to be a 1:1 electrolyte. Complete anion dissociation occurs for (**3**) in dmf (1:3 electrolyte), suggesting that the hydroxide bridge is still intact in solution, while for (**9**) partial dissociation occurs in dmf. The solution electronic spectrum of (**1**) in CH_3CN resembles that in the solid state while in dmf the shift of the visible absorption to lower energy may be largely due to solvent co-ordination. The distinct similarity between the solid-state and solution spectra (dmf) of (**2**) suggests that the basic binuclear structure of the complex remains intact in solution with a terminal bromine replaced by solvent. Compound (**9**) behaves in a similar fashion to (**1**) in dmf.

Electrochemistry.—The redox behaviour of antiferromagnetically coupled binuclear copper(II) complexes involving oxygen bridge groups generally consists of either one-step, two-electron transfer[32–34] or two-step, one-electron transfer[35–39] at negative potentials. In one recent case a two-step, one-electron redox process was observed for a hydroxo-bridged complex of a quadridentate naphthyridine ligand at positive potentials (0.16, 0.36 V *vs.* Ag/AgCl).[40] The binuclear, hydroxo-bridged complexes presented here are remarkable in that they all exhibit two-electron transfer at positive potentials. The electrochemical results are summarized in Table 3. The gross electrochemical behaviour of all the binuclear complexes is similar but is dependent on the choice of solvent and working electrode. A typical cyclic voltammogram, for compound (**1**), is shown in Figure 4. Peak separations for this compound (Pt electrode in CH_3CN) are virtually independent of scan rate indicating an almost reversible redox process. Compound (**9**) displays similar cyclic voltammetry. For the other complexes peak separations varied with scan rate implying quasi-reversible processes. In dmf (**1**) displays a quasi-reversible redox process but at a potential comparable with that in CH_3CN. For (**3**) rather poorly defined cyclic voltammograms were obtained with large values of ΔE_p indicating an irreversible redox process.

Coulometric studies (>0.2 V negative of $E_{\frac{1}{2}}$) indicate two-electron reduction for all the binuclear complexes studied. Typically the green or blue solutions (CH_3CN or dmf) became colourless after the passage of two electron equivalents. The visible spectrum of compound (**1**) (3×10^{-4} mol dm^{-3} in CH_3CN, 0.1 mol dm^{-3} $[NEt_4][ClO_4]$; Figure 5) showed a prominent absorption at 14 300 cm^{-1} which disappears on constant-potential electrolysis (+0.2 V) and reappears after reoxidation at +0.8 V. This redox cycle can be repeated several times without significant change in the visible absorption intensity.

The mononuclear complex (**4**), which is stable in acetonitrile, undergoes a non-reversible redox process in acetonitrile at a high positive potential indicating a likely instability of this species in solution with respect to the copper(II) state. This is confirmed by the rapid reaction of (**4**) with iodide in aqueous solution to produce the stable binuclear copper(I) species, $[Cu_2(ptpd)_2][I_3]_2$, and the spontaneous reduction of (**4**) in dmf to form a colourless solution.[41]

Although positive redox potentials have been reported for binuclear copper(II) complexes of cryptate ligands[42–44] and other ligands with mixed NS donor sets,[45] which have essentially magnetically isolated metal centres without oxygen bridge groups, examples of binuclear, hydroxo-bridged, copper(II) complexes exhibiting both antiferromagnetic exchange and positive redox potentials are rare[27,40] and the combination of these physical properties makes such systems very effective models for binuclear copper metalloprotein active sites. The high, positive redox potentials for these systems, which parallel those of some copper oxidase/oxygenase enzymes, suggest their possible catalytic activity in oxidase and oxygenase function. Preliminary initial velocity kinetic studies in tris(hydroxymethyl)aminoethane buffer in 40% aqueous acetonitrile (aqueous pH 7.35) on $[Cu_2(ptpd)(OH)Cl_3]\cdot EtOH$ (**1**) indicate significant catecholase activity involving the aerobic oxidation of 3,5-di-t-butylbenzene-1,2-diol. At a complex concentration of 1.5×10^{-5} mol dm^{-3} and substrate concentration varying from 2.2×10^{-3} to 7.3×10^{-5} mol dm^{-3} a Lineweaver Burk plot[46] gave a reasonable straight line with a maximum velocity, $V_{max.} = 3.2 \times 10^{-7}$ mol dm^{-3} s^{-1}, a rate constant for the breakdown of the catechol–complex intermediate, $k_p = 2.1 \times$

10^{-2} s^{-1}, and a Michaelis binding constant, $K_M = 3.4 \times 10^{-4}$ mol dm^{-3}. Further catalytic studies involving these, and other, binuclear complexes are in progress.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support for this study.

References

1 J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1969, 1408.
2 P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1969, 1415.
3 J. E. Andrew, P. W. Ball, and A. B. Blake, *Chem. Commun.*, 1969, 143.
4 P. W. Ball and A. B. Blake, *J. Chem. Soc., Dalton Trans.*, 1974, 852.
5 L. K. Thompson, V. T. Chacko, J. A. Elvidge, A B. P. Lever, and R. V. Parish, *Can. J. Chem.*, 1969, **47**, 4141.
6 A. B. P. Lever, L. K. Thompson, and W. M. Reiff, *Inorg. Chem.*, 1972, **11**, 104.
7 A. B. P. Lever, L. K. Thompson, and W. M. Reiff, *Inorg. Chem.*, 1972, **11**, 2292.
8 J. A. Doull and L. K. Thompson, *Can. J. Chem.*, 1980, **58**, 221.
9 J. C. Dewan and L. K. Thompson, *Can. J. Chem.*, 1982, **60**, 121.
10 D. V. Bautista, J. C. Dewan, and L. K. Thompson, *Can. J. Chem.*, 1982, **60**, 2583.
11 G. Marongiu and E. C. Lingafelter, *Acta Crystallogr., Sect. B*, 1982, **38**, 620.
12 G. Bullock, F. W. Hartstock, and L. K. Thompson, *Can. J. Chem.*, 1983, **61**, 57.
13 L. K. Thompson, *Can. J. Chem.*, 1983, **61**, 579.
14 F. W. Hartstock and L. K. Thompson, *Inorg. Chim. Acta*, 1983, **72**, 227.
15 L. K. Thompson, F. W. Hartstock, P. Robichaud, and A. W. Hanson, *Can. J. Chem.*, 1984, **62**, 2755.
16 L. K. Thompson, A. W. Hanson, and B. S. Ramaswamy, *Inorg. Chem.*, 1984, **23**, 2459.
17 L. K. Thompson, F. W. Hartstock, L. Rosenberg, and T. C. Woon, *Inorg. Chim. Acta*, 1985, **97**, 1.
18 G. Bullock, A. Cook, A. Foster, L. Rosenberg, and L. K. Thompson, *Inorg. Chim. Acta*, 1985, **103**, 207.
19 L. K. Thompson, T. C. Woon, D. B. Murphy, E. J. Gabe, F. L. Lee, and Y. Le Page, *Inorg. Chem.*, 1985, **24**, 4719.
20 A. M. Manotti Lanfredi, A. Tiripicchio, M. Ghedini, and G. De Munno, *Acta Crystallogr., Sect. B*, 1982, **38**, 1165.
21 M. Ghedini, G. De Munno, G. Denti, A. M. Manotti Lanfredi, and A. Tiripicchio, *Inorg. Chim. Acta*, 1982, **57**, 87.
22 G. De Munno, G. Denti, and P. Dapporto, *Inorg. Chim. Acta*, 1983, **74**, 199.
23 G. De Munno and G. Denti, *Acta Crystallogr., Sect. C*, 1984, **40**, 616.
24 P. Dapporto, G. De Munno, A. Sega, and C. Meali, *Inorg. Chim. Acta*, 1984, **83**, 171.
25 B. R. M. Reinhammer, *Biochim. Biophys. Acta*, 1972, **275**, 245.
26 N. Makino, P. McMahill, and H. S. Mason, *J. Biol. Chem.*, 1974, **249**, 6062.
27 S. K. Mandal, L. K. Thompson, and A. W. Hanson, *J. Chem. Soc., Chem. Commun.*, 1985, 1709.
28 F. L. Urbach, in 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1981, vol. 13, p. 73 and refs. therein; E. I. Solomon, in 'Copper Proteins,' ed. T. G. Spiro, Wiley, New York, 1981, p. 41; K. Lerch, in 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1981, vol. 13, p. 143.
29 A. Hirsch and D. Orphanos, *Can. J. Chem.*, 1965, **43**, 2708.
30 A. B. P. Lever, E. Mantovani, and B. S. Ramaswamy, *Can. J. Chem.*, 1971, **49**, 1957.
31 E. J. Gabe, F. L. Lee, L. K. Thompson, and S. K. Mandal, unpublished work.
32 D. E. Fenton, R. R. Schroeder, and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 1931.
33 D. E. Fenton and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1978, **100**, 6367.
34 S. K. Mandal and K. Nag, *Inorg. Chem.*, 1983, **22**, 2567.
35 A. W. Addison, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 899.
36 R. R. Gagné, C. A. Koval, and T. J. Smith, *J. Am. Chem. Soc.*, 1977, **99**, 8367.
37 R. R. Gagné, R. P. Kreh, and J. A. Dodge, *J. Am. Chem. Soc.*, 1979, **101**, 6917.
38 S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429.
39 J. Deo Cabral, M. F. Cabral, M. McCann, and S. M. Nelson, *Inorg. Chim. Acta*, 1984, **86**, L15.
40 W. R. Tikkanen, C. Kruger, K. D. Bomben, W. L. Jolly, W. C. Kaska, and P. C. Ford, *Inorg. Chem.*, 1984, **23**, 3633.
41 L. K. Thompson and S. K. Mandal, unpublished work.
42 A. H. Alberts, R. Annunziata, and J-M. Lehn, *J. Am. Chem. Soc.*, 1977, **99**, 8502.
43 J-P. Gisselbrecht, M. Gross, A. H. Alberts, and J-M. Lehn, *Inorg. Chem.*, 1980, **19**, 1386.
44 Y. Agnus, R. Louis, J-P. Gisselbrecht, and R. Weiss, *J. Am. Chem. Soc.*, 1984, **106**, 93.
45 J-M. Latour, D. Limosin, and P. Rey, *J. Chem. Soc., Chem. Commun.*, 1985, 464.
46 A. Ault, *J. Chem. Educ.*, 1974, **51**, 381.

Received 8th October 1985; *Paper* 5/1742