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Binuclear Copper(II) Complexes of some Potentially Sexadentate Phthalazine Hydrazone Ligands

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Binuclear copper(II) complexes of three potentially sexadentate phthalazine hydrazone ligands, obtained by reacting 1,4-dihydrazinophthalazine with an appropriate aldehyde, are reported, in which variable terminal donor substituents include the phenol (DPSI), N-methyl imidazole (DPIM) and pyridine (PHP) groups. For the phenol substituted ligand (DPSI) the phenol residues are sufficiently acidic that in most cases this ligand behaves as a dianion. Hydroxy bridged structures are proposed in almost all cases based on analytical, infrared and magnetic data. Reduced magnetic moments are observed for all compounds indicating antiferromagnetically coupled copper(II) centres and in six cases magnetic moments of <0.5 BM are observed. The copper(II) centres appear to have distorted square planar stereochemistries in the systems which involve two metals bound to each ligand. In one case involving the copper chloride complex of DPIM a polynuclear system is proposed involving three metals per ligand.

Introduction

The phthalazine or pyridazine group has been shown by a number of researchers to provide the binucleating centre for numerous binuclear transition metal complexes of cobalt(II), cobalt(III), nickel(II), copper(II) and zinc(II) salts [1–14]. In all these systems the ligands are tetradentate N_4 donors in which nitrogen donor substituents are bound to the ring sites adjacent to the diazine ring nitrogen atoms. 1,4-dihydrazinophthalazine (DHPH; Fig. 1) is a reactive intermediate, which acts as a tetradentate binucleating ligand in its own right [1–4], and reacts with appropriate aldehydes to form the corresponding hydrazones [15]. A sexadentate binucleating ligand DHPHPY (henceforth abbreviated PHP) has been synthesized by reaction of DHPH and pyridine-2-carboxaldehyde and the structure of a binuclear nickel(II) complex reported [16]. In another case DHPH was shown to form an octadentate binucleating macrocyclic ligand in the formation of a binuclear nickel(II) complex in the presence of acetone [17].

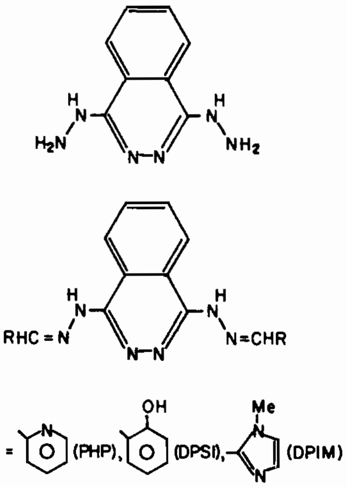

Fig. 1. The ligands PHP, DPSI and DPIM.

The proximity of the two diazine nitrogen atoms results in the two metal centres in such systems being close together with metal–metal separations falling in the range 3.0–3.8 Å [2, 5, 9, 14, 16]. For the two structurally documented systems involving nickel with DHPH [2] and PHP [16] metal–metal separations are found to be 3.79 Å and 3.60 Å respectively. In these complexes five-membered chelate rings are formed, while in other pyridyl amino-phthalazine systems involving copper, which have six-membered chelate rings, much smaller metal–metal separations (3.0–3.2 Å) are observed [9, 14].

No examples of binuclear copper(II) complexes of DHPH or sexadentate ligands like PHP, have been reported. That DHPH is a hydrazine derivative (a reducing agent) would explain the difficulty involved in synthesizing copper(II) complexes of such a ligand. In this report we describe some binuclear copper(II) complexes of DPSI (1,4-dihydrazinophthalazine bis-(salicylaldimine)), DPIM (1,4-dihydrazinophthalazine

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bis(1′-methyl-2′-imidazolecarboxaldimine) and PHP 1,4-dihydrazinophthalazine bis(2′-pyridinecarboxaldimine)) (Fig. 1).

Experimental

Ligands

DPSI

The synthesis of this ligand was carried out according to the literature procedure [15] but after several attempts this method could not be reproduced as indicated. The following modified procedure was employed.

1,4-dihydrazinophthalazine [18] (3.8 g, 20 mmol) and salicylaldehyde (4.9 g, 40 mmol) were reacted in ethanol (400 ml) under reflux for 7 h. Decolourizing charcoal was added and the yellow-orange solution filtered and allowed to stand overnight. Sparkling orange crystals (*A*) formed which were filtered, washed with an ethanol/ether mixture and air dried (Yield 5 g, 63%; mp 118–122 °C). The volume of the mother liquor was reduced giving a yellow powder (*B*) (m.p. 214–218 °C). *A*. *Anal.* Calcd. for $C_{22}H_{18}N_6O_2 \cdot 3H_2O$: C, 62.6; H, 6.16; N, 19.9. Found: C, 62.2; H, 5.21; N, 19.9%. Mass spectrum, major mass peaks (m/e (relative intensity)) 398(40) P, 305(28), 279(31), 245(4), 229(12), 186(64), 129(30), 121(23), 105(12), 102(22), 96(15), 91(100), 86(21).

Compound *B* did not correspond to the desired product and so far its identity has not been elucidated. If the literature procedure is followed (reflux 1 hour) the yield of product *A* is very low and the major product is the yellow component *B*. Also the melting point of *A* is much lower than that reported in the literature.

DPIM

1,4-dihydrazinophthalazine (3.8 g, 20 mmol) and N-methylimidazole carboxaldehyde [19] (4.4 g, 40 mmol) were refluxed together in methanol (300 ml) for 3 h. Yellow crystals formed on cooling which were filtered washed with pet. ether, dried under vacuum and recrystallized from ethanol (yield = 1.6 g, 22%; mp 244–248 °C). *Anal.* Calcd. for $C_{18}H_{18}N_{10}$: C, 57.8; H, 4.81; N, 37.4. Found: C, 57.8; H, 4.82; N, 37.8%. Mass spectrum major mass peaks (m/e (relative intensity)) 374(3) (P), 373(7), 292(100), 265(8), 251(4), 222(8), 185(19), 129(12), 123(12), 109(47), 108(64), 95(99), 82(66), 67(13).

$[Cu_2(DPIM\text{-}H)(OH)](NO_3)_2 \cdot 2CH_3OH$ (I)

DPIM (0.30 g, 1.1 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.55 g, 2.3 mmol) were both dissolved in hot methanol and the solutions mixed. A blood red colouration was obtained and on cooling reddish brown crystals formed. The product was filtered, washed with methanol and ether and dried under vacuum. Other complexes of DPIM were prepared similarly.

$[Cu_2(DPSI\text{-}H)(OH)](NO_3) \cdot CH_3OH$ (IX)

DPSI (0.50 g, 1.3 mmol) was dissolved in hot methanol and the solution filtered. $Cu(NO_3)_2 \cdot 3H_2O$ (0.60 g, 2.5 mmol) was dissolved in hot methanol and the solutions mixed. An olive green precipitate formed immediately, which was filtered, washed with methanol, ether and dried under vacuum. Other complexes of DPSI were prepared similarly.

$[Cu_2(PHP)(OH)](ClO_4)_3 \cdot 0.25CH_3CH_2OH$ (X)

The ligand PHP was not isolated but was synthesized *in situ* before adding the solution of metal salt.

1,4-dihydrazinophthalazine (1.0 g, 5.3 mmol) was stirred in absolute ethanol (100 ml) with warming. Pyridine-2-carboxaldehyde (1.2 g, 11 mmol) was added and the mixture refluxed until the DHPH dissolved. $Cu(ClO_4)_2 \cdot 6H_2O$ (4.9 g, 13 mmol) was dissolved in absolute ethanol (50 ml) and the solution added to the hot solution of the ligand. A red-brown solid formed almost immediately. The mixture was heated with stirring for 10 min and the solid filtered, washed with ethanol, ether and dried under vacuum.

Other complexes of PHP were prepared in a similar fashion. Crystalline products were only obtained in a few cases and were not found to be suitable for X-ray analysis.

Physical Measurements

Electronic spectra were recorded with a Cary 17 spectrometer and infrared spectra with a Perkin-Elmer Model 283 spectrometer. Magnetic susceptibilities were obtained at room temperature by the Faraday method using a Cahn Model #7600 Faraday Magnetic Susceptibility system, coupled to a Cahn gram electrobalance. Mass spectra were run using a V.G. Micromass 7070 HS with a direct insertion probe. Microanalyses were carried out by Canadian Microanalytical Service, Vancouver (C, H, N). Metal analyses were determined by atomic absorption with a Varian Techtron AA-5, after digestion of the samples in concentrated HNO_3 or aqua regia.

Results and Discussion

In our previous studies involving antiferromagnetically coupled binuclear copper(II) complexes the ligands involved were tetradentate disubstituted pyridylphthalazines, in which the metal centres were brought into close proximity with metal–metal separations falling in the range 3.0–3.2 Å [6, 11–14, 20]. In almost all cases triple bridges were found between the five-coordinate copper(II) centres, including a diazine (N_2) bridge, a hydroxy bridge and an anionic entity as the third bridge group. Variation of this anionic group was used to tune the dimensions of the binuclear centre with corresponding changes in the exchange integral [20].

Various models have been suggested for the coupled binuclear copper protein centres, including systems with two and three histidine groups per metal centre, but a concensus of opinion favours a single oxygen atom (as hydroxide or phenoxide) as the dominant bridging entity responsible for the strong antiferromagnetic coupling observed in *e.g.* oxy-hemocyanin (*Megathura crenulata*) [21, 22] and *Rhus vernicifera* laccase [21].

The pyridylphthalazine ligands form six-membered chelate rings with relatively small metal–metal separations. However disubstituted phthalazines and pyridazines involving five-membered chelate rings were shown to generate systems with much larger metal–metal separations [2, 5, 16, 20]. The ligands DPIM, DPSI and PHP (Fig. 1) were chosen for study because they should form five-membered chelate rings, thus having the potential for the formation of systems with large metal–metal separations, and also because they present alternatives to the other model ligands already studied (N_4 donors) by offering each metal three potential donor sites.

The ligand DPIM is previously unreported and reacts readily with copper(II) salts to give highly coloured products. The copper nitrate complex (*I*) has two nitrate groups, which are both ionic (a single $\nu_1 + \nu_4$ nitrate combination band at 1760 cm^{-1} corresponds to ionic nitrate [23]), and a hydroxy bridge according to analytical and infrared data (Table III). The charge deficiency associated with two nitrate groups can be rationalized in terms of two hydroxides or a deprotonated ligand and one hydroxide. Molecular models indicate that a sexadentate ligand accommodating two four-coordinate metal centres bridged by a single hydroxide group would provide a structure involving a minimum of strain and that inclusion of a second hydroxide bridge, involving five-coordinate copper centres, would be a highly strained system. Electronic spectral bands (Table II) can be associated with a distorted square planar system and the very low room temperature magnetic moment, indicative of a strongly antiferromagnetically coupled system, supports the presence of a single hydroxy bridge.

The perchlorate complex (*II*) appears to have the same basic structural unit (Fig. 2) but with a neutral ligand. Again the low magnetic moment (0.46 BM) supports a single hydroxy bridged species and the electronic spectral bands at 15400 and 19200 cm^{-1} can be associated with distorted square copper centres. The intense band at 22700 cm^{-1} is associated with a charge transfer absorption (π–π^*) and it is of interest to note that this band is missing in the nitrate

TABLE I. Analytical Data.

	Compound	Colour	Found(%)				Calcd(%)			
			C	H	N	Cu	C	H	N	Cu
I	$[Cu_2(DPIM\text{-}H)(OH)](NO_3)_2\cdot 2CH_3OH$	Red-brown	33.9	3.15	24.1	17.5	34.0	3.69	23.8	18.0
II	$[Cu_2(DPIM)(OH)](ClO_4)_3\cdot CH_3OH\cdot 2H_2O$	Brown	26.0	2.61	16.1	14.1	26.0	3.07	15.9	14.4
III	$[Cu_3(DPIM)(OH)_2Cl_4]\cdot 2CH_3OH$	Red-brown	29.7	2.35	17.4	23.4	29.8	3.48	17.4	23.7
IV	$[Cu_2(DPSI\text{-}H)Cl]Cl\cdot 1.5H_2O$	Green	42.3	2.65	13.2	19.4	42.5	3.05	13.5	20.6
V	$[Cu_2(DPSI\text{-}H)Br]Br\cdot H_2O$	Olive-green	37.6	2.39	11.9	18.5	37.7	2.57	12.0	18.1
VI	$[Cu_2(DPSI\text{-}H)(OMe)]$	Dark-brown	49.5	2.84	14.9	22.0	49.8	3.43	15.1	22.9
VII	$[Cu_2(DPSI\text{-}H)(OH)](BF_4)\cdot CH_3OH$	Green-brown	42.4	3.10	12.7	18.8	41.9	3.19	12.7	19.3
VIII	$[Cu_2(DPSI\text{-}H)(OH)](ClO_4)\cdot CH_3OH$	Olive-green	41.3	2.92	12.5	18.6	41.1	3.12	12.5	18.9
IX	$[Cu_2(DPSI\text{-}H)(OH)](NO_3)\cdot CH_3OH$	Olive-green	43.6	2.93	15.3	20.5	43.5	3.31	15.5	20.0
X	$[Cu_2(PHP)(OH)](ClO_4)_3\cdot 0.25CH_3CH_2OH$	Red-brown	30.0	2.20	13.7	15.1	29.9	2.24	13.6	15.5
XI	$[Cu_2(PHP\text{-}H)(OH)(CH_3COO)_2]0.5H_2O$	Red-brown	45.4	3.23	17.4	19.6	45.1	3.75	17.5	19.9

TABLE II. Electronic (Mull Transmittance) Spectra and Magnetic Moments.

	Compound	d–d (cm^{-1})†	μBM(RT)
I	$[Cu_2(DPIM\text{-}H)(OH)](NO_3)_2\cdot 2CH_3OH$	[11900], [15600], 18900, [20000]	0.44
II	$[Cu_2(DPIM)(OH)](ClO_4)_3\cdot CH_3OH\cdot 2H_2O$	[15400], [19200], 22700	0.46
III	$[Cu_3(DPIM)(OH)_2Cl_4]\cdot 2CH_3OH$	12000, 23300	1.37
IV	$[Cu_2(DPSI\text{-}H)Cl]Cl\cdot 1.5H_2O$	8900, 10500, 23800	1.41
V	$[Cu_2(DPSI\text{-}H)Br]Br\cdot H_2O$	9100, 10300, 23300	1.51
VI	$[Cu_2(DPSI\text{-}H)(OMe)]$	8900, 10100, [19400], 26300	1.11
VII	$[Cu_2(DPSI\text{-}H)(OH)](BF_4)\cdot CH_3OH$	9300, 10500, [19200], [25000]	0.35
VIII	$[Cu_2(DPSI\text{-}H)(OH)](ClO_4)\cdot CH_3OH$	9300, 10300, [18900], [25000]	0.34
IX	$[Cu_2(DPSI\text{-}H)(OH)](NO_3)\cdot CH_3OH$	9350, 10500, [19000], [25000]	0.49
X	$[Cu_2(PHP)(OH)](ClO_4)_3\cdot 0.25CH_3CH_2OH$	20000, 23800	0.48
XI	$[Cu_2(PHP\text{-}H)(OH)(CH_3COO)_2]0.5H_2O$	10900, [14300], 21000	1.57

† [ ] = shoulder.

TABLE III. Infrared Spectra.

	Compound	Infrared (cm^{-1})
I	$[Cu_2(DPIM\text{-}H)(OH)](NO_3)_2\cdot 2CH_3OH$	3490sh, 3400 (OH, CH_3OH) 1760 ($\nu_1 + \nu_4NO_3$), 340 (Cu–O)
II	$[Cu_2(DPIM)(OH)](ClO_4)_3\cdot CH_3OH\cdot 2H_2O$	3500br, (OH, H_2O, CH_3OH), 1080 (ClO_4^-), 342 (Cu–O)
III	$[Cu_3(DPIM)(OH)_2Cl_4]\cdot 2CH_3OH$	3540 (OH), 3400 (CH_3OH), 320 (Cu–Cl), 340 (Cu–O)
IV	$[Cu_2(DPSI\text{-}H)Cl]Cl\cdot 1.5H_2O$	3330 (NH), 532 (Cu–O), 318 (Cu–N), 267 (Cu–Cl)
V	$[Cu_2(DPSI\text{-}H)Br]Br\cdot H_2O$	3480sh(H_2O), 3380 (NH), 531 (Cu–O), 318 (Cu–N), 257 (Cu–Br)
VI	$[Cu_2(DPSI\text{-}H)(OMe)]$	535 (Cu–O), 402 (Cu–O), 319 (Cu–N)
VII	$[Cu_2(DPSI\text{-}H)(OH)](BF_4)\cdot CH_3OH$	3600 (OH), 3520 (CH_3OH), 530 (Cu–O), 403 (Cu–O), 320 (Cu–N)
VIII	$[Cu_2(DPSI\text{-}H)(OH)](ClO_4)\cdot CH_3OH$	3550 (OH), 3480 (CH_3OH), 535 (Cu–O), 402 (Cu–O), 321 (Cu–N)
IX	$[Cu_2(DPSI\text{-}H)(OH)](NO_3)\cdot CH_3OH$	3630 sh (OH) 3480sh (CH_3OH) 1745 ($\nu_1 + \nu_4NO_3$), 532 (Cu–O), 404 (Cu–O), 320 (Cu–N)
X	$[Cu_2(PHP)(OH)](ClO_4)_3\cdot 0.25CH_3CH_2OH$	3600sh (OH), 1090 (ClO_4^-), 1020 (pyr), 315 (Cu–N)
XI	$[Cu_2(PHP\text{-}H)(OH)(CH_3COO)_2]0.5H_2O$	3500 (OH) 1590, 1420 (CH_3COO^-), 1025 (pyr), 303 (Cu–N)

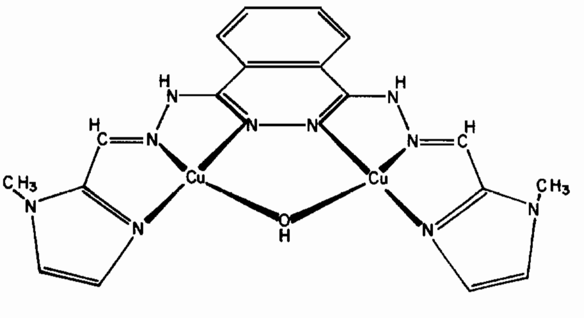

Fig. 2. Proposed structure for the binuclear cation in *II*.

spectrum. In *I* the equivalent band appears at 20000 cm^{-1}. A shift to lower energy of a π–π^* type charge transfer absorptions has been shown in the past to be the result of anion formation in ligands of this sort by proton loss [6]. DPIM itself exhibits an intense charge transfer absorption at 24700 cm^{-1}. Infrared absorptions (Table III) observed around 340 cm^{-1} for both compounds are associated with copper–oxygen stretch involving the hydroxide bridge.

The chloride complex (*III*) is clearly not a simple derivative and analytical data indicate the presence of three metals per ligand. A reduced magnetic moment indicates a spin coupled system, which presumably involves a hydroxy bridged structure, as indicated by infrared absorption at 3540 cm^{-1}. The charge transfer absorption for this system at 23300 cm^{-1} suggests the presence of a neutral ligand. Structural arrangements involving three metal centres can be envisaged but without X-ray crystallographic evidence they are just speculation.

Complexes of the ligand DPSI clearly involve the coordination of DPSI in its dianionic form in which proton loss has occurred at both phenolic oxygen atoms. The chloro- and bromo-derivatives (*IV*, *V*), which appear not to involve hydroxide bridges, are characterized by having slightly reduced magnetic moments, indicative of weakly exchanged systems, in which a halogen bridge could be the dominant pathway for spin exchange. The infrared spectra of *IV* and *V* are very similar and no bands are observed indicative of a hydroxy bridge. Absorptions at about 530

cm^{-1} are, however, associated with copper–oxygen stretch to the phenoxide residues. Other bands are tentatively assigned in Table III.

The electronic spectra of *IV* and *V* are characterized by rather low energy absorptions in the range 9000–10000 cm^{-1}, which are clearly d–d in origin. Unlike the case of DPIM, which would form only five-membered chelate rings, DPSI allows the formation of one six-membered chelate ring per metal centre when it behaves as a sexadentate ligand. The enhanced flexibility of these six-membered chelate rings involving the phenoxide groups could allow the formation of a triple bridge between the metal centres. However molecular models suggest that it would still be rather strained. A tetrahedrally distorted four-coordinate structure is therefore suggested for compounds *IV* and *V*, involving a halogen bridge, in keeping with the rather low energy d–d bands.

Compounds *VII, VIII* and *IX* have certain common features in their infrared (Table III) and electronic spectra (Table II) which suggest that structurally they are very similar. Infrared bands in the range 3550–3630 cm^{-1} are associated with OH stretch in a hydroxy bridged structure. In all cases the ligand behaves as a dianion, presumably by loss of phenolic protons, while the inorganic anion remains uncoordinated. The role of methanol, in these and other systems, is seen as a solvent molecule filling some crystal lattice site. d–d bands for these compounds, which are almost identical, are similar to those observed for *IV* and *V*, but shifted slightly to higher energy. The structural implication is again of a somewhat tetrahedrally distorted four-coordinate system involving a CuN_2O_2 chromophore (Fig. 3).

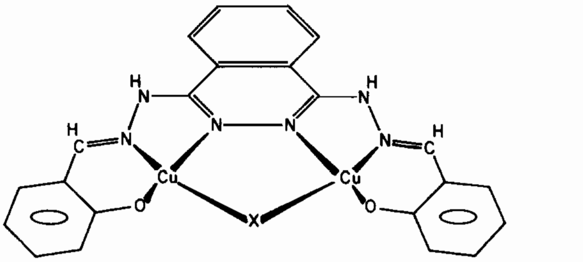

Fig. 3. Proposed structure for the binuclear cations in *IV* (*X* = Cl), *V* (*X* = Br), *VII–IX* (*X* = OH).

Magnetically a comparison of *IV* and *V* with *VII, VIII* and *IX* should reveal some marked differences, because of the proposed halogen bridges on the one hand versus the hydroxy bridges in the other group of compounds. Slightly reduced moments are observed for the chloro- and bromo-complexes, in keeping with the presence of halogen bridges, while the very low moments associated with compounds *VII–IX* support the proposed hydroxy bridged structures. Binuclear copper(II) systems with single hydroxy bridges have been shown to exhibit moderate to strong antiferromagnetic exchange, depending on the bridge angle and the d orbital ground state [12–14, 20, 24–27]. For systems with a $d_{x^2-y^2}$ ground state, involving tetradentate phthalazine ligands, a linear relationship has been observed between the oxygen bridge angle and the exchange integral. Also, for the same systems, a linear relationship exists between room temperature magnetic moment and oxygen bridge angle [20]. Previously we have shown that for a room temperature magnetic moment of about 0.6 BM with an oxygen bridge angle of 125°, in a square pyramidal system, the exchange integral (–2J) is around 800 cm^{-1} [20]. In view of the very low moments associated with *VII–IX* a rather large bridge angle is anticipated with strong antiferromagnetic exchange. Such arguments would also apply to compounds *I, II* involving the ligand DPIM.

Compound *VI*, which was prepared by reaction of DPSI with copper acetate in methanol, appears to have no carboxylate residue according to infrared spectra and this is confirmed by reaction of DPSI with copper butyrate in methanol. Exactly the same compound is produced with an identical infrared spectrum. Analytical data indicate the presence of one additional carbon residue over and above the carbon complement of the ligand and this is associated with a methoxide group. The ligand therefore appears to coordinate as a trianionic entity involving the loss of both phenolic protons and one NH proton. The low room temperature moment suggests that the methoxide is a bridging entity but by comparison with compounds *VII–IX* the oxygen bridge angle is probably somewhat smaller.

The only literature report of a binuclear complex of PHP is the chloro-bridged nickel derivative described by Palenik [16], in which the ligand is almost planar. However considerable distortion occurs in the equatorial plane of the six-coordinate nickel(II) centres. The geometrical constraints of the nitrogen donor framework (N_3) at each metal centre, which involves two five-membered rings, is such that N–Ni–N angles of less than 80 degrees are observed. It is anticipated that a similar situation would exist with copper as the metal centre and that for DPIM a distorted system would also be expected. For DPSI systems, which involve one six-membered chelate ring, such distortions would presumably be smaller.

The perchlorate complex of PHP (*X*) appears to be a hydroxy bridged species involving ionic perchlorate. A pyridine ring breathing vibration is observed in the infrared at 1020 cm^{-1} indicative of coordinated pyridine groups [6], and suggests that the ligand coordinates in a sexadentate fashion. High energy absorption in the electronic spectrum supports a distorted square planar stereochemistry and the very low room temperature magnetic moment supports the infrared evidence for a hydroxy bridge. A fairly large oxygen-bridge angle would therefore be anticipated. A structural representation for this system is shown in Fig. 4. (acetate groups removed).

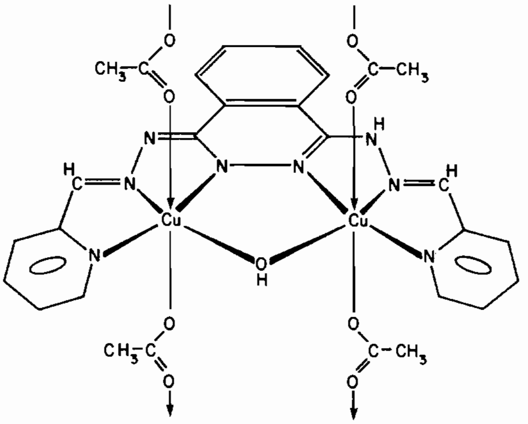

Fig. 4. Proposed structure for *XI*.

The acetate complex (*XI*), unlike its DPSI counterpart, contains carboxylate residues. Infrared bands at 1420 and 1590 cm^{-1}, which are absent in the spectra of *X*, are associated with symmetric and antisymmetric carboxyl stretch in a bridging acetate [28]. Although infrared data also suggest the presence of a hydroxy bridge analytical data indicate the presence of only one such bridge in addition to the two acetate groups. The implication here is that the ligand behaves as an anionic entity through proton loss. A rather low energy charge transfer absorption at 21000 cm^{-1} indicates that the ligand in *XI* is significantly different from that in *X*, in which there is no doubt that it is neutral. The slightly reduced magnetic moment of 1.57 BM cannot be associated with a structure similar to that in *e.g.* *X* and *II*, and probably also involves a smaller oxygen bridge angle at the hydroxy bridge. In keeping with the spectral and magnetic evidence a polymeric six-coordinate structure is suggested for this compound involving a basic in plane entity similar to that in *X*, but with axial bridging acetate groups binding the planar units together in a stacked arrangement (Fig. 4).

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