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Copper complexes of polyfunctional phthalazines. Mononuclear and polynuclear derivatives

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Mononuclear, binuclear, and trinuclear copper(II) complexes of the tetradentate ligands 1,4-di(2′-pyridyl) aminophthalazine (PAP) and 1,4-di(4′-methyl-2′-pyridyl) aminophthalazine (PAP4Me) and binuclear complexes of the tetradentate ligand 1,4-di(6′-methyl-2′-pyridyl) aminophthalazine (PAP6Me) are reported. In a series of binuclear carboxylate derivatives carboxylate bridges exist between copper centres in all cases and in some cases oxygen bridges (hydroxide or methoxide) are indicated. In all other polynuclear derivatives hydroxide bridges are anticipated on the basis of analytical, spectral, and magnetic data. The ligands exist as anionic groups in some binuclear carboxylate derivatives while in the other polynuclear systems neutral ligands are found. In reactions in aqueous solution protonated mononuclear derivatives are obtained for both PAP and PAP4Me in cases where solutions of the metal salts are inherently acidic, followed by polynuclear, neutral ligand complexes which form when the pH increases. Mononuclear protonated complexes are not obtained with PAP6Me, where steric factors may prevent the formation of such derivatives. Low magnetic moments (1.1–1.5 BM) are observed for most hydroxy bridged complexes while even lower values (<0.70 BM) are observed for two binuclear complexes of PAP6Me, indicating the possibility of strong antiferromagnetic exchange between metal centres. A preliminary X-ray investigation of the complex $[Cu_2(PAP4Me)(OH)(NO_3)_2(H_2O)_2]NO_3$ indicates a triple bridged binuclear structure including a bidentate nitrate bridge and a hydroxide bridge with an oxygen bridge angle of 115.2°.

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On a préparé les complexes mono-, bi- et trinucléaires du cuivre(II) des ligands tétradentates di(pyridyl 2′)-1,4 aminophtalazine (PAP) et di-(méthyl-4′ pyridyl-2′)-1,4 aminophtalazine (PAP4Me) et les complexes binucléaires du ligand tétradentate di(méthyl-6′ pyridyl-2′)-1,4 aminophtalazine (PAP6Me). Dans une série de dérivés carboxylates binucléaires, il existe dans tous les cas des ponts carboxylates entre les centres cuivre et, dans certains cas, on trouve des ponts oxygènes (hydroxyde ou méthylate). En se basant sur des données analytiques, spectrales et magnétiques, on prévoit qu'il existera des ponts hydroxydes dans tous les autres dérivés polynucléaires. Les ligands existent sous forme de groupes anioniques dans certains carboxylates binucléaires tandis que, dans d'autres systèmes polynucléaires, on trouve des ligands neutres. Lorsque les solutions de sels métalliques sont intrinsèquement acides, on obtient des dérivés mononucléaires protonés avec le PAP et le PAP4Me en solution aqueuses et des complexes polynucléaires de ligands neutres lorsque le pH augmente. On n'obtient pas de complexes mononucléaires protonés avec le PAP6Me alors que des facteurs stériques empêchent la formation de tels dérivés. On a observé de faibles moments magnétiques (1.1–1.5 BM) pour la plupart des complexes ayant un pont hydroxyde tandis qu'on observe des valeurs plus faibles (< 0.70 BM) pour deux complexes binucléaires du PAP6Me; ceci indique qu'il existe une possibilité d'un fort échange antiferromagnétique entre les centres métalliques. Une étude préliminaire du complexe $[Cu_2(PAP4Me)(OH)(NO_3)_2(H_2O)_2]NO_3$ par cristallographie de rayons X indique une structure binucléaire triplement pontée incluant un pont nitrate bidentate et un pont hydroxyde avec un angle du pont oxygène de 115,2°.

[Traduit par le journal]

Introduction

Binucleating ligands containing just nitrogen donor atoms have received some attention in recent years and have been based largely on substituted "diazine" type units. Polyfunctional ligands derived from hydrazine (1–3), pyrazole (4–8), pyridazine (4, 9–11), and phthalazine (4, 9, 11, 12–19) form transition metal complexes in which the metals are brought into close proximity because of the presence of the N_2, diazine, fragments in these systems. Antiferromagnetic exchange between the adjacent metal centres has been demonstrated in some of these complexes (4, 11, 13, 15, 16, 18) and catecholase activity has been shown with binuclear copper complexes of the binucleating ligand 1,4-di(2′-pyridyl) aminophthalazine (PAP) (Fig. 1). In a recent paper (21) binuclear copper complexes of the ligand 3,6-bis(2′-pyridyl) pyridazine are described and an X-ray structure of the chloro-derivative reveals a double bridge involving the pyridazine N_2 and a hydroxide. Binuclear complexes involving macrocyclic, nitrogen-containing ligands have also been synthesized (14, 22).

PAP has been shown to bind preferentially to two metal centres forming binuclear complexes with copper, cobalt, nickel, and zinc salts (13, 15, 16, 18, 19). Antiferromagnetic exchange exists between the metal centres in cobalt, nickel, and copper complexes of PAP (13, 15, 16, 18). PAP appears to be quite sensitive to protonation, even in mildly acidic solution, and as a result of the inherent acidity of aqueous and alcoholic solutions of certain commercially available metal salts, protonated

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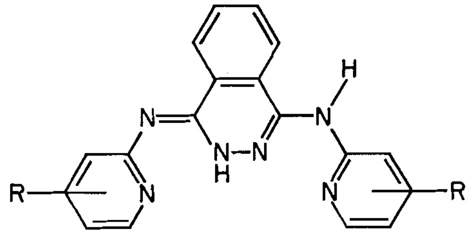

FIG. 1. PAP (R = H), PAP4Me (R = 4 methyl), PAP6Me (R = 6 methyl).

mononuclear (1:2) complexes are obtained as initial products, in certain reactions, followed by binuclear or polynuclear derivatives containing neutral ligand (18, 19).

In this paper we describe some copper complexes of PAP, which have not been previously reported, and some copper complexes of two closely related pyridyl phthalazines: 1,4-di(4′-methyl-2′-pyridyl) aminophthalazine (PAP4Me) and 1,4-di(6′-methyl-2′-pyridyl) aminophthalazine (PAP6Me). These ligands are previously unreported. Protonated mononuclear, neutral ligand binuclear and polynuclear complexes are obtained for PAP4Me, these systems bearing a close resemblance to counterparts with PAP itself, while for PAP6Me only binuclear complexes are obtained. The absence of any protonated mononuclear (1:2) complexes of the pyridyl phthalazine involving a methyl substituent in the 6-position on the pyridine ring is no doubt due to steric constraints imposed by such groups. However, in keeping with the general ability of PAP type ligands to act as weak bases, protonated ligand salts are produced in certain reactions involving PAP6Me. Preliminary X-ray structural details of the complex $[Cu_2(PAP\text{-}4Me)(OH)(NO_3)_2(H_2O)_2]NO_3$ are also reported.

Experimental

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. Nuclear magnetic resonance spectra were run as solutions in deuterochloroform using a Bruker WP80 spectrometer and mass spectra were run using a Hitachi-Perkin Elmer RMU-6E with the 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.

Ligands

PAP was prepared as described previously (13) but can also be prepared conveniently by the following procedure.

1,4-Di(4′-methyl-2′-pyridyl) aminophthalazine (PAP4Me)

1,3-Di(4′-methyl-2′-pyridyl) iminoisoindoline was prepared by fusing phthalonitrile (12.8 g, 0.100 mol) and 2-amino-4-methylpyridine (21.6 g, 0.200 mol) and maintaining a temperature of 220°C until ammonia evolution ceased (approximately 12 h). Extraction of the solid, which formed on cooling, into ethanol gave yellow crystals on recrystallization (yield = 24.2 g; 75%) (mp 164°C) (lit. 165–166°C, ref. 22).

The isoindoline (15.0 g, 0.050 mol) was dissolved in methanol (400 mL) under reflux, 85% hydrazine hydrate (8.0 mL) added, and the mixture refluxed for 15 h, or until ammonia evolution had essentially ceased. Filtration and reduction in volume led to the formation of a yellow crystalline product, which was recrystallized from ethanol (yield = 13.2 g, 84%) and dried at 80°C under vacuum for 3 h (mp 178°C). *Anal.* calcd. for $C_{20}H_{18}N_6$: C 70.2, H 5.26, N 24.6; found: C 70.2, H 5.45, N 24.3. Mass spectrum, major mass peaks (*m/e* (relative intensity)) 342 (100) P, 327 (10), 235 (23), 222 (25), 93 (68), 92 (95); ^1H nmr ($CDCl_3$) (σ(relative intensity)) 2.33 (45) (singlet, CH_3), 6.68 (15) (doublet, pyridine H_5), 7.10 (7) (singlet, pyridine H_3), 7.7 (36) (multiplet, 1NH, *o*-phenylene H_β, pyridine H_6), 8.1 (15) (multiplet, *o*-phenylene H_α), 8.75 (7) (broad singlet, 1NH). The observation of two different types of NH indicates that the ligand exists in chloroform solution in the tautomeric form illustrated in Fig. 1. Also the absence of a symmetric set of resonances attributable to a symmetrically disubstituted benzene ring indicates the presence of a tautomeric form of the ligand in which the phthalazine moiety is not bisected by a mirror plane. In the infrared spectrum two bands attributable to NH stretch are observed at 3270 and 3200 cm^{-1}, again supporting two different NH groups.

1,4-Di(6′-methyl-2′-pyridyl) aminophthalazine (PAP6Me)

PAP6Me was prepared in the same way as PAP4Me and obtained as a yellow crystalline solid which was recrystallized from ethanol and dried at 80°C, under vacuum, for 3 h (yield isoindoline = 41%; yield phthalazine = 83%) (mp 158–161°C). *Anal.* calcd. for $C_{20}H_{18}N_6$: C 70.2, H 5.26, N 24.6; found: C 69.9, H 5.37, N 24.3. Mass spectrum, major mass peaks (*m/e* (relative intensity)) 342 (100) P, 235 (24), 93 (84), 92 (90); ^1H nmr ($CDCl_3$) (σ(relative intensity)) 2.52 (30) (singlet, methyl), 6.76 (10) (doublet, pyridine H_5), 7.52 (10) (doublet, pyridine H_3), approximately 7.8 (30) (poorly defined multiplet, *o*-phenylene H_α, H_β, pyridine H_4), 8.75 (5) (NH). The NH resonance is very broad and an estimate of its integrated intensity suggests only one proton. Location of the second NH proton was unsuccessful, but it may be buried beneath the rather broad envelope of resonances in the range 6.7–8.05. The indication of two different types of NH suggests that the ligand exists in chloroform in the tautomeric form shown in Fig. 1. Also, unlike the isoindoline, whose nmr spectrum clearly shows an AA′BB′ splitting pattern associated with a symmetrically *o*-disubstituted benzene ring, the phthalazine shows an asymmetric set of resonances due to the fused benzene ring protons, indicating an unsymmetrical ligand involving two different types of NH. In the mull infrared spectrum a sharp, single absorption at 3400 cm^{-1} suggests the possibility of just one type of NH in the solid state and a symmetrical tautomer probably involving hydrogen atoms bound to just the exocyclic nitrogen atoms.

Copper complexes

$[Cu(PAPH)_2(NO_3)_2](NO_3)_2.0.5H_2O$ (I), $[Cu_3(PAP)_2(OH)_2(NO_3)_2](NO_3)_2.4H_2O$ (II)

PAP (1.00 g; 3.18 mmol) was added to a solution of $Cu(NO_3)_2.3H_2O$ (0.770 g; 3.19 mmol) dissolved in water (200 mL) and the mixture refluxed for 2 h. The resulting green solution was filtered and allowed to stand at room temperature in a loosely covered beaker. Buff-coloured crystals (**I**) were obtained and after several days this product was filtered off, washed with ethanol and ether, and dried under vacuum and the mother

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liquor allowed to evaporate further. A second crop of buff crystals was obtained and the process repeated. A third crop of crystals contained **I** plus a green crystalline product (**II**) and finally green crystals (**II**) were obtained as the sole product in the fourth crop. The green product was recrystallized from water, washed with ethanol and ether, and dried under vacuum.

Pairs of products, including in each case a protonated mononuclear derivative and a polynuclear neutral ligand derivative, were obtained in a similar fashion from the reaction of $Cu(ClO_4)_2.6H_2O$ (**III**, buff; **IV**, green) with PAP in methanol or water and reactions of $Cu(NO_3)_2.3H_2O$ (**XV**, buff–yellow; **XVI**, blue), $Cu(ClO_4)_2.6H_2O$ (**XVII**, green–yellow; **XVIII**, green), and $Cu(BF_4)_2.6H_2O$ (**XIX**, green–yellow; **XX**, green) with PAP4Me in aqueous solution. In certain cases recrystallization of a product was effected from methanol and solvate molecules are found in the complex.

[Cu₂(PAP)(p-tolylSCH₂COO)₄].1.5H₂O (IX)

$CuCO_3.Cu(OH)_2.H_2O$ (0.800 g; 3.35 mmol) and *p*-tolylthioacetic acid (2.34 g; 12.7 mmol) were added to methanol (150 mL) and the mixture refluxed for 15 min. PAP (1.00 g; 3.18 mmol) was added and the mixture refluxed for 1 h and the resulting green solution filtered. Reduction in volume of the solution did not produce a product and so the solvent was completely removed and the resulting green solid extracted with $MeOH/CHCl_3$ (50/50). On standing a green powder was formed, which was filtered, washed with ether, and dried under vacuum.

The other copper thio- and sulfoxy-carboxylate complexes (**V–VIII**, **X**, **XI**) were prepared similarly using stoichiometric amounts of copper carbonate and the appropriate carboxylic acid and obtained as green solids.

[Cu₂(PAP4Me)(OH)Cl₃].H₂O (XII)

PAP4Me (1.00 g; 2.92 mmol) was added to a solution of $CuCl_2.2H_2O$ (3.23 g; 18.9 mmol) dissolved in water (100 mL) and the mixture refluxed for 1 h. A green precipitate formed which was filtered, washed with water, recrystallized from water, and dried under vacuum at room temperature.

The corresponding bromo-complex (**XIII**) and the copper chloride and copper bromide complexes of PAP6Me (**XXI**, **XXII**) were prepared similarly and obtained as green crystalline solids.

[Cu₂(PAP4Me)(CH₃COO)₂(OH)].H₂O (XIV)

PAP4Me (1.00 g; 2.92 mmol) was added to a solution of cupric acetate (1.17 g; 2.96 mmol) dissolved in ethanol (300 mL) and the mixture refluxed for 45 min. The volume of the resulting green solution was reduced to approximately 100 mL and allowed to stand. A powdery khaki-green product was obtained which was recrystallized from methanol to give a khaki-green solid. The product was filtered off, washed with methanol and ether, and dried under vacuum at room temperature.

The copper acetate complex of PAP6Me (**XXIII**) was prepared similarly and obtained as a khaki-green powder.

[Cu₂(PAP6Me)(OH)(NO₃)₂]NO₃ (XXIV)

PAP6Me (0.500 g; 1.46 mmol) was dissolved under reflux in ethanol (100 mL). $Cu(NO_3)_2.3H_2O$ (0.688 g; 2.92 mmol) was dissolved in a mixture of ethanol (10 mL) and water (5 mL) and the solution added to the solution of the ligand. The resulting dark green solution was refluxed for 1 h and allowed to stand. A dark green product formed which was filtered, washed with ethanol and ether, and recrystallized from methanol.

[PAP6MeH₂](ClO₄)₂ (XXV), [Cu₂(PAP6Me)(OH)(H₂O)₂](ClO₄)₃.0.5H₂O (XXVI)

PAP6Me (0.500 g; 1.46 mmol) was dissolved under reflux in ethanol (20 mL) and the solution added to a solution of $Cu(ClO_4)_2.6H_2O$ (1.08 g; 2.92 mmol) dissolved in water (30 mL). The resulting dark green solution was refluxed for 15 min and cooled. A light yellow powder formed (0.26 g) which was filtered off (**XXV**), washed with ethanol, and dried under vacuum. Reduction in volume of the mother liquor produced a dark green solid (0.48 g) which was filtered off (**XXVI**), washed with ethanol, and dried under vacuum.

Satisfactory analytical data have been obtained for these complexes and are reported in Table 1, which has been placed in the Depository of Unpublished Data.[2]

Results and discussion

The new ligands described in this paper (PAP4Me, PAP6Me; Fig. 1) are analogues of the parent pyridyl phthalazine (PAP) in which methyl groups have been introduced at the 4- and 6-positions of the pyridine ring. They are all prepared by a common synthetic route in which ring expansion of the isoindoline precursor is effected simply by reaction with hydrazine hydrate. The synthetic route to the isoindoline precursors involves the direct reaction of phthalonitrile and the appropriate 2-aminopyridine at high temperatures for periods of up to 12 h followed by extraction into ethanol. This direct fusion method, which we have used routinely for a number of years, provides good yields of the disubstituted isoindolines and is a more efficient procedure than previously reported syntheses involving phthalonitrile (23, 24) and 1,3-diiminoisoindoline (25) as starting materials. The synthesis of the 5-methyl isoindoline by this route was recently reported by Addison and coworkers (26).

Characterization of the complexes

Previously reported copper complexes of PAP have included binuclear systems involving two metals bound to the same ligand (13) and mononuclear derivatives in which two bidentate ligands are bound to the same metal (19). Polynuclear derivatives involving three copper centres and a binuclear derivative involving two metals bound simultaneously to two tetradentate ligands have also been reported (19). In a series of binuclear copper carboxylate derivatives of PAP the pK_a of the corresponding carboxylic acid determined whether or not the ligand was neutral or anionic. For acids whose pK_a is greater than 3.8 complexes of the type $[Cu_2(PAP-H)(RCOO)_3]$ (PAP–H indicates anionic PAP involving loss of a proton) are formed, whereas for acids whose pK_a is less than 3.8 complexes of the type $[Cu_2(PAP)(RCOO)_4]$, involving neutral ligand, are formed (13).

In an attempt to involve sulphur centres in the coordination sphere of the metal in binuclear systems of this sort, carboxylate complexes involv-

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ing sulphur-containing carboxylic acids were synthesized. Instead of isolating the copper carboxylate itself the binuclear carboxylate complexes (**V**–**XI**) were synthesized by reacting ligand, copper carbonate, and the appropriate acid in a suitable solvent. Both 1:2:3 and 1:2:4 stoichiometries (ligand:metal:carboxylic acid) were used in synthesizing these compounds. However, two distinct compounds were obtained only in the case of phenylthioacetic acid and since a neutral ligand is indicated for **V**, in which three carboxylate groups are found, the remaining anionic charge can exist as either methoxide or hydroxide. The absence of any infrared absorption associated with OH suggests the former assignment. For the remaining systems only one compound formed regardless of the chosen stoichiometry.

The pK_a values of the thio- and sulfoxyacetic acids fall in the range 2.6–3.5 and if the previous criterion for the type of complex formed were to apply then only derivatives of the type [Cu_2(PAP)-$(RCOO)_4$] or those involving neutral ligand should be formed. Neutral ligand derivatives are confirmed for all the carboxylate complexes in the solid state, with the possible exception of **VII**, by the presence of at least one charge transfer band at 27000 cm^{-1} or higher (13). Although compound **VII** has a solid state charge transfer band at 27500 cm^{-1}, analytical and other data suggest an anionic derivative.

Previous studies have shown that the presence of an infrared band above 1000 cm^{-1}, associated with the ring breathing mode of the pyridine ring in PAP, indicates the coordination of this group to the metal centres (13). Absorptions in the range 1017–1025 cm^{-1} (Table 2) for compounds **V**–**IX** indicate the involvement of the pyridine rings in coordination and suggest that PAP behaves as a tetradentate ligand. Similar absorptions could not be observed for compounds **X**, **XI** because of interfering bands associated with the sulfoxy groups.

Infrared absorptions found in the solid state in the range 1626–1345 cm^{-1} for all the carboxylate complexes can be associated with both terminal and bridging carboxylate groups (13). Typically two absorptions occur around 1600 cm^{-1}, the one at higher energy being associated with the antisymmetric vibration of a terminal carboxylate while the lower energy absorption is associated with the antisymmetric mode of a bridging carboxylate. Other carboxylate bands occurring around 1400 cm^{-1} are assigned to symmetric vibrations associated with both bridging and terminal carboxylates, although distinction between these bands is difficult. A comparison of the solid state spectra in this region with those obtained in chloroform solution (Table 2) indicates the possible disproportionation of certain species in solution. For compounds **VI** and **IX**, which contain four carboxylate groups, a new carboxylate band appears around 1700 cm^{-1}, which is not observed in the solid state (**VIII** was not soluble enough in chloroform to be studied), while the other carboxylate absorptions remain approximately the same. Since absorptions of this sort around 1700 cm^{-1} can be associated with the free carboxylic acid itself it is suggested that these neutral tetracarboxylate derivatives dissociate via loss of one molecule of the appropriate carboxylic acid to form tricarboxylates, containing anionic ligand, in solution. This is supported by the observation of only one charge transfer absorption around 24000 cm^{-1} associated with anionic PAP. There was no infrared evidence to indicate the involvement of the sulfur or sulfoxy groups in coordination to the metal centres in these complexes.

The solid state electronic spectra of the carboxylate complexes (Table 3) are in general characterized by a major absorption in the range 14500–16400 cm^{-1} accompanied in many cases by a low energy shoulder. The spectra are very similar to those reported previously for related tri- and tetracarboxylate derivatives which were assigned square pyramidal coordination geometries (13). In the solid state charge transfer bands are observed in all cases at 27000 cm^{-1} or above, signalling the presence of neutral ligand. These data can be rationalized reasonably in all cases except compound **VII** where analytical results indicate three carboxylate functions and the absence of a hydroxide group, thus suggesting an anionic ligand. Certainly in solution in chloroform this species appears to contain anionic ligand.

Magnetic moments, measured at room temperature (Table 3), appear normal for compounds **VI**, **VIII**, and **IX**, being in excess of the spin only value for copper(II), and indicate that any antiferromagnetic exchange between the metal centres is small. Efficient bridge exchange groups, e.g. oxygen centres, are therefore considered to be absent in these systems (27–29). Considerably reduced room temperature moments are observed for compounds **V**, **X**, and **XI** in keeping with the proposal that in addition to having phthalazine and carboxylate bridges the copper centres are also bridged by oxygen groups, viz. a methoxide in **V** and hydroxides in **X** and **XI**. For compound **VII**, a slightly reduced room temperature moment signals weaker exchange and the absence of an oxygen bridge. Proposed structures for the carboxylate complexes are given in Fig. 2. Compound **VII** may be a four-coordinate derivative but could also be five-

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TABLE 2. Infrared data (cm^{-1})

Compound	νCN	Other
I, $[Cu(PAPH)_2(NO_3)_2](NO_3)_2.0.5H_2O$	1619, 1625, 1635, 1664	1748, 1759, 1765 ($\nu_1 + \nu_4$, NO_3^-) 996, 1014(pyr)
II, $[Cu_3(PAP)_2(OH)_2(NO_3)_2](NO_3)_2.4H_2O$	1610, 1640	1764, 1756, 1749 ($\nu_1 + \nu_4$, NO_3^-) 3400(OH, H_2O), 3280(NH), 1002, 1021(pyr)
III, $[Cu(PAPH)_2](ClO_4)_4.0.5H_2O$	1628, 1631, 1655	1110(ClO_4^-), 3380(NH) 1007(pyr)
IV, $[Cu_3(PAP)_2(OH)_2(MeOH)_2](ClO_4)_4$	1618, 1637	1065, 1100 (ClO_4^-) 3340(NH), 3525(OH, MeOH)
V, $[Cu_2(PAP)(PhSCH_2COO)_3(OMe)].H_2O$	1617, 1641	1025(pyr), 1400, 1585, 1604($RCOO^-$), 3300(NH) [a] 1365(sh), 1400(sh), 1600, 1615(sh)($RCOO^-$)
VI, $[Cu_2(PAP)(PhSCH_2COO)_4].H_2O$	1614, 1640(sh)	1025(pyr), 1355(sh), 1398, 1593, 1626($RCOO^-$), 3300(NH), 3400, 3470(H_2O) [a] 1365, 1400(sh), 1595, 1610, 1700($RCOO^-$)
VII, $[Cu_2(PAP)(o\text{-tolylSCH}_2COO)_3]$	1640	1018(pyr), 1400(sh), 1594, 1616($RCOO^-$) [a] 1400(sh), 1594, 1615($RCOO^-$)
VIII, $[Cu_2(PAP)(m\text{-tolylSCH}_2COO)_4]$	1633	1017(pyr), 1356, 1396, 1586, 1607($RCOO^-$)
IX, $[Cu_2(PAP)(p\text{-tolylSCH}_2COO)_4].1.5H_2O$	1640	1018(pyr), 1367, 1405(sh), 1591, 1615($RCOO^-$) [a] 1400(sh), 1595, 1605, 1725($RCOO^-$)
X, $[Cu_2(PAP)(OH)(PhS(O)CH_2COO)_3]$	1640(sh)	1345(sh), 1410(sh), 1592, 1615($RCOO^-$) [a] 1352, 1590(sh), 1617($RCOO^-$)
XI, $[Cu_2(PAP)(OH)(p\text{-tolylS(O)CH}_2COO)_3].H_2O$	1640(sh)	1395(sh), 1400(sh), 1590, 1612 [a] 1400(sh), 1590(sh), 1620
XII, $[Cu_2(PAP4Me)(OH)Cl_3].H_2O$	1618, 1643	3360(NH), 3560(OH) 321(Cu—Cl)
XIII, $[Cu_2(PAP4Me)(OH)Br_3]$	1620, 1640	3350, 3460(NH), 3610(OH) 230(Cu—Br)
XIV, $[Cu_2(PAP4Me)(OH)(CH_3COO)_2(H_2O)]$	1644	1360, 1404(sh), 1590, 1629($RCOO^-$), 3300(NH) [a] 1360, 1400(sh), 1593, 1628($RCOO^-$)
XV, $[Cu(PAP4MeH)_2](NO_3)_4$	1621, 1635, 1655, 1660(sh)	1755 ($\nu_1 + \nu_4$, NO_3^-), 3280(NH)
XVI, $[Cu_2(PAP4Me)(OH)(H_2O)_2(NO_3)_2]NO_3$	1626, 1645	1751, 1753, 1766, 1784 ($\nu_1 + \nu_4$, NO_3^-), 3300(NH), 3500(H_2O), 3580(OH), 290(Cu—O)
XVII, $[Cu(PAP4MeH)_2](ClO_4)_4.2MeOH$	1620, 1637, 1640	1060, 1100(ClO_4^-), 3330(NH), 3580(MeOH)
XVIII, $[Cu_3(PAP4Me)_2(OH)_2(H_2O)_2](ClO_4)_4.MeOH$	1622, 1645	1065, 1100(ClO_4^-), 3330(NH), 3590(H_2O), 3650(OH)
XIX, $[Cu(PAP4MeH)_2](BF_4)_4.H_2O$	1620, 1640, 1662	1060(BF_4^-), 3360(NH), 3560(sh), 3620(H_2O)
XX, $[Cu_3(PAP4Me)(OH)_2(H_2O)_2](BF_4)_4$	1630(sh), 1643	1060(BF_4^-), 3320(NH), 3550(H_2O), 3600(OH)
XXI, $[Cu_2(PAP6Me)(OH)Cl_3].2H_2O$	1612, 1630	3380(NH), 3450, 3520(H_2O), 3620(OH) 286, 301(Cu—Cl)
XXII, $[Cu_2(PAP6Me)(OH)Br_3]$	1612, 1624	3400(NH), 3620(OH) 255, 277(Cu—Br)
XXIII, $[Cu_2(PAP6Me)(CH_3COO)_3].0.5H_2O$	1612, 1633	1404, 1585($RCOO^-$), 3290(NH), 3410(H_2O) 305(sh), 320(Cu—O) [a] 1360, 1380, 1575, 1720
XXIV, $[Cu_2(PAP6Me)(OH)(NO_3)_2]NO_3$	1614, 1633	1724, 1750, 1757 ($\nu_1 + \nu_4$, NO_3^-), 3320(NH), 3480(OH), 285, 305(Cu—O)
XXV, $[PAP6MeH_2](ClO_4)_2$	1618, 1622, 1645(sh), 1650, 1660(sh)	1080(ClO_4^-), 3320(NH)
XXVI, $[Cu_2(PAP6Me)(OH)(H_2O)_2](ClO_4)_3.0.5H_2O$	1615, 1632	1070, 1095(ClO_4^-), 3350(NH), 3430, 3500(sh)(H_2O), 3680(OH) 265(Cu—O)

[a] Solution in chloroform.

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TABLE 3. Electronic spectra (cm^{-1}) (log ε) and magnetic moments

	Compound		*d–d*	CT	μ (BM)$_{Cu}$ (room temperatur
I,	$[Cu(PAPH)_2(NO_3)_2](NO_3)_2.0.5H_2O$	[a]	[15700]18200	27800	1.90
II,	$[Cu_3(PAP)_2(OH)_2(NO_3)_2](NO_3)_2.4H_2O$	[a]	[11700], [14800]16900	27400	1.32
III,	$[Cu(PAPH)_2](ClO_4)_4.0.5H_2O$	[a]	[13300][15600]	28500	1.80
IV,	$[Cu_3(PAP)_2(OH)_2(MeOH)_2](ClO_4)_4$	[a]	[10500][14800]16700	28200	1.43
V,	$[Cu_2(PAP)(PhSCH_2COO)_3(OMe)].H_2O$	[a] [f]	[10800]14800 [10900](1.94)14500(2.31)	28900 24600(4.25)	1.30
VI,	$[Cu_2(PAP)(PhSCH_2COO)_4].H_2O$	[a] [f]	15900 [10900](2.05)14300(2.32)	28900 24450(4.20)	1.85
VII,	$[Cu_2(PAP)(o\text{-tolylSCH}_2COO)_3]$	[a] [f]	[10800]15400 14900(2.26)	[24400]27500 24600(4.18)25600(4.17)	1.62
VIII,	$[Cu_2(PAP)(m\text{-tolylSCH}_2COO)_4]$	[a]	[13900]16400	28200	1.83
IX,	$[Cu_2(PAP)(p\text{-tolylSCH}_2COO)_4].1.5H_2O$	[a] [f]	14500 [10900](2.01)14900(2.34)	28600 24500(4.23)	1.78
X,	$[Cu_2(PAP)(OH)(PhS(O)CH_2COO)_3]$	[a] [f]	15200 14900(2.20)	[24000][27300] 24600(4.04)26900(4.07)	1.50
XI,	$[Cu_2(PAP)(OH)(p\text{-tolylS(O)CH}_2COO)_3].H_2O$	[a] [f]	[11000]14900 15000(2.19)	[24400]27000 24600(4.02)27400(4.10)	1.32
XII,	$[Cu_2(PAP4Me)(OH)Cl_3].H_2O$	[a]	[13200]15900	29400	1.43
XIII,	$[Cu_2(PAP4Me)(OH)Br_3]$	[a] [b]	16100 10600(1.53)15800(1.83)	28200 29400(3.25)	1.20
XIV,	$[Cu_2(PAP4Me)(OH)(CH_3COO)_2(H_2O)]$	[a] [c]	17400 [17600](1.93)	24700 25400(2.98)	1.42
XV,	$[Cu(PAP4MeH)_2](NO_3)_4$	[a] [c]	[14800]18200	28600 28100(4.44)	2.10
XVI,	$[Cu_2(PAP4Me)(OH)(H_2O)_2(NO_3)_2]NO_3$	[a] [c]	16300 16500(1.96)	28200 29600(3.14)	1.12
XVII,	$[Cu(PAP4MeH)_2](ClO_4)_4.2MeOH$	[a] [c]	[14700][18300]23800	28600 28900(4.49)	1.90
XVIII,	$[Cu_3(PAP4Me)_2(OH)_2(H_2O)_2](ClO_4)_4.MeOH$	[a] [b]	[10600][14800]16900 [11000][14000]16100	[28600] 27000(4.14)	1.54
XIX,	$[Cu(PAP4MeH)_2](BF_4)_4.H_2O$	[a]	[17100]	28200 28700(4.45)	1.90
XX,	$[Cu_3(PAP4Me)(OH)_2(H_2O)_2](BF_4)_4$	[a] [b]	[10500][14600]16500 [10500](1.84)[14000](2.12) 15600(2.14)	29000 29300(4.56)	1.31
XXI,	$[Cu_2(PAP6Me)(OH)Cl_3].2H_2O$	[a] [b]	14800 14800	27800 28900	0.68
XXII,	$[Cu_2(PAP6Me)(OH)Br_3]$	[a] [b]	17200	[27800] 29100(4.14)	0.66
XXIII,	$[Cu_2(PAP6Me)(CH_3COO)_3].0.5H_2O$	[a] [c]	[16000] 17200(2.37)	23800 24700(4.19)	1.60
XXIV,	$[Cu_2(PAP6Me)(OH)(NO_3)_2]NO_3$	[a] [b]	16400 14500(2.11)	[28600] 29100(4.14)	1.20
XXV,	$[PAP6MeH_2](ClO_4)_2$	[a]		[26700]27800	
XXVI,	$[Cu_2(PAP6Me)(OH)(H_2O)_2](ClO_4)_3.0.5H_2O$	[a] [c]	[14000]16700 16500(2.12)	[28900] [25300]	1.30

[a] Mull transmittance.
[b] Solution spectra in water.
[c] Solution spectra in methanol.
[d] Solution spectra in nitromethane.
[e] Solution spectra in ethanol.
[f] Solution spectra in chloroform.

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coordinate via intermolecular association involving the terminal carboxylates as was observed previously (13).

In a previous paper (19) we reported the formation of two different complexes from the reaction of copper tetrafluoroborate and PAP in aqueous solution: a mononuclear derivative, $[Cu(PAPH)_2(H_2O)_2](BF_4)_4$, containing protonated bidentate ligand, and a polynuclear, neutral ligand derivative which was formulated as a trinuclear system, $[Cu_3(PAP)_2(OH)_2](BF_4)(BF_3OH)_3.5H_2O$. The ease with which PAP became protonated, even in weakly acidic solutions, was shown to be the reason why such a mixture of compounds was formed. Surprisingly a similar situation arose in the reactions between copper nitrate and copper perchlorate with PAP (approximately 0.1 *M* solutions of copper nitrate and copper perchlorate have pH values of 3.7 each).

Buff-coloured protonated derivatives (**I**, **III**) were obtained as initial products from the reactions of copper nitrate and copper perchlorate with PAP in aqueous solution. The presence of up to four CN stretching vibrations in the infrared (Table 2) can be attributed to the presence of protonated PAP (19). The observtion of three nitrate combination bands (30) can be interpreted in terms of the presence of both ionic and monodentate nitrate and in keeping with the electronic spectrum (Table 3), it seems reasonable to assume a tetragonally distorted six-coordinate structure for **I** involving two axially bound monodentate nitrate groups and two in-plane bidentate protonated PAP ligands. The perchlorate derivative (**III**) appears to have an analogous square planar structure without the involvement of any axial ligand. Magnetic moments for these compounds are typical of mononuclear copper derivatives.

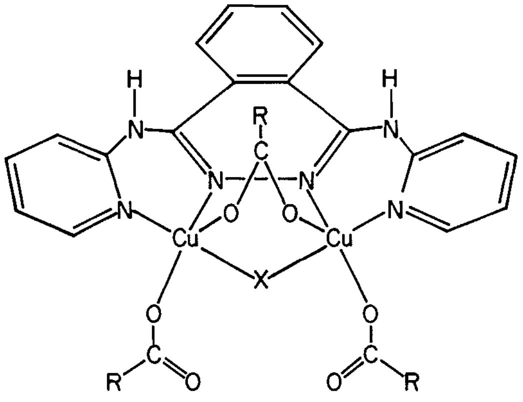

FIG. 2. Proposed structures for **V** (X = OMe), **X**, **XI** (X = OH), **VI**, **VIII**, **IX** (X = RCOO).

Additional green products (**II**, **IV**) are also obtained from both reaction mixtures, which do not contain protonated ligand. Two CN bands are observed in the infrared in each case, typical of neutral PAP. Nitrate combination bands indicate the presence of both ionic and monodentate nitrate in **II**, while for **IV** the ν_3 perchlorate vibration, although it is slightly split, probably indicates ionic perchlorate. Pyridine ring breathing absorptions are observed for **II** in excess of 1000 cm^{-1}, indicative of the presence of tetradentate PAP (13), while for **IV** such absorptions are hidden by the perchlorate band. Elemental analyses suggest a metal-to-ligand ratio of 3:2 for **II** and **IV**, which requires the presence of two hydroxy groups to complete a charge balance. Rather broad infrared absorptions at 3400 cm^{-1} (**II**) and 3525 cm^{-1} (**IV**) are associated with water (**II**) and methanol (**IV**) and bridging hydroxy groups, probably involved in hydrogen bonding.

The electronic spectra of **II** and **IV** are very similar in the solid state involving three major absorptions and resemble very closely the spectrum of $[Cu_3(PAP)_2(OH)_2](BF_4)(BF_3OH)_3.5H_2O$ (19), suggesting a similar species. In general the binuclear copper complexes of PAP involve five-coordinate copper centres and only one major *d–d* band is observed in this region of the spectrum (13). The three prominent absorptions observed for **II** and **IV** therefore suggest the possible presence of more than one different stereochemistry for the copper centres in these systems. A reasonable suggestion for the structures of **II** and **IV** is illustrated in Fig. 3 in which two tetradentate ligands are bound simultaneously to three copper centres in a trinuclear arrangement. The central copper is six-coordinate being bound to the other two copper centres via phthalazine and hydroxy bridges. The outer two copper atoms are probably four-coordinate, the fourth coordination site being occupied by monodentate nitrates in **II** and methanol molecules in **IV**. Such a system can be rationalized spectroscopically by assuming that the highest energy *d–d* component can be associated with the two distorted square planar copper centres and that the two lower energy components can be asso-

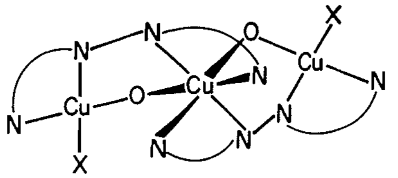

FIG. 3. Proposed structures for the cation in **II** (X = NO_3), **IV** (X = MeOH), **XVIII** and **XX** (X = H_2O).

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ciated with a *cis*-N_4O_2 six-coordinate copper centre. Magnetic moments per copper centre for **II** and **IV** are quite low, indicating significant spin exchange, which would again support the presence of hydroxy bridges between the copper centres.

PAP4Me, which involves methyl substituents at the 4-position on the pyridine ring, forms similar copper complexes to those of PAP. This is perhaps not so surprising since substituents at the 4-position would not be expected to exert any unusual electronic or steric effects. Compounds **XII** and **XIII** are analogous to the PAP counterparts with hydroxy and halogeno bridges between the copper centres and reduced room temperature moments indicative of antiferromagnetic exchange (13, 31) (Fig. 2; X = OH, RCOO = halide). However, the moments are somewhat lower than those of the PAP analogues (Cl, $\mu = 1.60$ BM; Br, $\mu = 1.66$ BM) (13) which may indicate some structural modification at the binuclear centre in the systems.

The acetate complex **XIV** contains two acetate groups, according to elemental analysis, and has a low energy charge transfer absorption (13) indicative of the presence of anionic ligand (it is assumed that PAP and its simple methylated analogues will exhibit similar π–π^* absorptions). In keeping with these data a hydroxy bridge is also implicated and although there is weak infrared evidence for the presence of such a group the low magnetic moment does indicate such a bridge. The high energy single *d*–*d* absorption (Table 3), present both in the solid state and solution, is consistent with a five-coordinate derivative. In the infrared, absorptions are observed both in the solid state and in chloroform solution consistent with the presence of both bridging and terminal carboxylate groups. A rather broad weak absorption around 3500 cm^{-1} is associated with the hydroxide bridge and water molecule. Considering all the data a reasonable structure would involve a terminal carboxylate on one copper centre, a carboxylate and a hydroxide bridge, and a water molecule bound to the other copper centre (Fig. 2, X = OH, one terminal carboxylate replaced by H_2O). The formation of a hydroxy derivative in this case is seen as a result of the presence of water in the ethanol used to prepare the complex.

As in the case of PAP, two nitrate complexes are obtained. **XV** is clearly a protonated, mononuclear derivative which has a pseudo square planar structure according to both infrared and electronic spectral data. The presence of only one nitrate combination band at 1755 cm^{-1} signifies the presence of ionic nitrate only. The blue neutral ligand species **XVI** appears to be a binuclear derivative, unlike its PAP counterpart. Infrared data suggest a hydroxy bridged species involving coordinated water and the complex absorption in the combination ($\nu_1 + \nu_4$) nitrate region suggests more than one type of nitrate group. The bands at 1751 and 1766 cm^{-1} can be associated with monodentate nitrate and the band at 1753 cm^{-1} with ionic nitrate. However, the high energy band at 1784 cm^{-1} may be associated with a bridging bidentate nitrate (30).

Preliminary X-ray studies on this system (32) confirm the binuclear structure (Fig. 4) (Table 4) involving tetradentate PAP4Me, a hydroxide bridge, and a bidentate nitrate bridge. A second nitrate group is bound to Cu(2) with a bond length to O(2) of 2.034 Å. The interatomic distance Cu(2)—O(14) of 2.738 Å may indicate the nitrate group to be a weakly bound unsymmetrical bidentate chelating ligand giving rise to a distorted six-coordinate tetragonal structure around Cu(2). In a review of metal nitrate bonding (33) it is suggested that the nitrate group may be considered bidentate if the difference in the two closest metal–oxygen distances does not exceed 0.7 Å. The coordination geometry around Cu(1) can be considered to be tetragonal, six-coordinate with a long axial bond to O(16) of a water molecule. Of particular significance in the structure is the large bridge angle at O(1) (115.2°) and the metal–metal separation (3.138 Å). Full details of this structure will be published elsewhere.

We have recently examined the structure and magnetism of a series of complexes, $[Cu_2(PAP)(OH)X_3]$ (X = Cl, Br, IO_3) (34), and find that the binuclear centre can be tuned by varying the non-hydroxy bridge. The Cu—O—Cu bridge angle

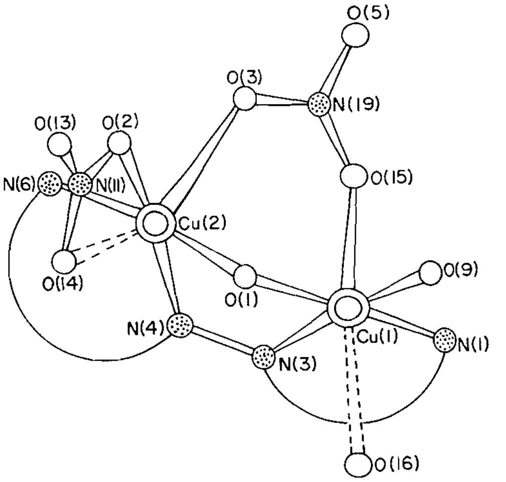

FIG. 4. X-ray structure for the cation in $[Cu_2(PAP4Me)(OH)(NO_3)_2(H_2O)_2]NO_3$.N(1)N(3)N(4)N(6) represents the ligand PAP4Me; O(9)H_2O, O(16)H_2O ($R = 0.035$).

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TABLE 4. Selected bond lengths and bond angles for $[Cu_2(PAP\text{-}4Me)(OH)(H_2O)_2(NO_3)_2]NO_3$ (R = 0.035)

Bond	Length (Å)	Bonds	Angle (deg)
Cu(1)—N(1)	1.951	Cu(1)—O(1)—Cu(2)	115.2
Cu(1)—N(3)	2.022	O(15)—Cu(1)—O(16)	169.2
Cu(1)—O(1)	1.857	O(1)—Cu(1)—N(1)	174.3
Cu(1)—O(9)	2.009	N(3)—Cu(1)—O(9)	173.5
Cu(1)—O(15)	2.428	O(15)—Cu(1)—O(1)	95.5
Cu(1)—O(16)	2.617	O(3)—Cu(2)—O(14)	129.8
Cu(1)—Cu(2)	3.138	O(2)—Cu(2)—N(4)	168.8
		N(6)—Cu(2)—O(1)	171.3
		O(3)—Cu(2)—O(1)	94.8
Cu(2)—N(4)	2.042		
Cu(2)—N(6)	1.965		
Cu(2)—O(1)	1.858		
Cu(2)—O(2)	2.034		
Cu(2)—O(3)	2.330		
Cu(2)—O(14)	2.738		

is increased from 100° to 114° on replacing a chlorine bridge by an iodate bridge and the exchange integral increases from $-2J = 201$ to $-2J = 335$ cm^{-1}. Room temperature moments for these two systems are 1.66 BM (Cl) and 1.39 BM (IO_3). The low room temperature moment (1.12 BM) observed for **XVI** is consistent with the larger oxygen bridge angle for this nitrate bridged system and suggests the possibility of enhanced antiferromagnetic exchange.

The reaction of copper perchlorate and tetrafluoroborate with PAP4Me parallels the same reactions involving PAP. In both cases protonated, mononuclear derivatives, **XVII**, **XIX**, are produced which have pseudo-square planar structures involving bidentate, protonated PAP4Me. Also polynuclear derivatives, **XVIII** and **XX**, are obtained as final products in these reactions, which are analogues of **II** and **IV**, and are assumed to have the same basic structure (Fig. 3) but involving coordinated water at the four-coordinate copper centres.

Normal magnetic moments are observed for **XVII** and **XIX**, as would be expected for mononuclear derivatives, while the reduced moments observed for **XVIII** and **XX** are indicative of polynuclear species involving antiferromagnetic exchange. Three major absorptions are observed in the mull transmittance spectra of **XVIII** and **XX**, which can be associated with two different copper stereochemistries. Infrared data confirm the presence of protonated ligand in the mononuclear complexes **XVII** and **XIX** by the appearance of more than two νCN bands while for the polynuclear systems just two such bands are observed.

The introduction of a methyl group in the four position of the pyridine ring does not appear to have caused any major differences between the coordination chemistry of PAP and PAP4Me other than perhaps the formation of a binuclear nitrate complex with PAP4Me. However, a 6-methyl substituted ligand, in which the methyl group would be in a much better position to sterically influence the binuclear centre, might produce different complexes or analogues in which the dimensions of the binuclear centre might change.

Dark green binuclear products are obtained with copper chloride and bromide with PAP6Me (**XXI**, **XXII**) which appear to be analogues of the corresponding PAP and PAP4Me derivatives. Infrared absorptions observed at 3620 cm^{-1} in both cases are indicative of the presence of a hydroxy bridge and other bands in the range 250–300 cm^{-1} can be attributed to copper–halogen bonds. One major visible absorption is observed in each case which can be attributed to five-coordinate copper(II). On the surface these two compounds appear to have structures similar to their PAP and PAP4Me analogues (Fig. 2; X = OH, RCOO = halogen). However, the very low room temperature magnetic moments indicate the likelihood of enhanced magnetic exchange in these systems which can be seen as a result of the 6-methyl groups exerting a steric effect which forces the pyridine rings away from the binuclear centre thus increasing the metal–metal separation and the oxygen bridge angle. However, we await structural data and variable temperature magnetic studies to confirm this.

The copper acetate complex of PAP6Me (**XXIII**) appears to be similar to the acetate complex of PAP itself. A low energy charge transfer band (Table 3) indicates the presence of anionic ligand both in the solid state and in solution, while a single visible absorption, observed in the solid state spectrum at 16000 cm^{-1}, is consistent with a five-coordinate derivative. In methanol solution the *d–d* absorption is observed at 17200 cm^{-1}, 1200 cm^{-1} higher than in the solid state, suggesting the possibility of a change in stereochemistry. Carboxylate bands are observed in the infrared in the solid state (Nujol mull) at 1404 and 1585 cm^{-1} which can be associated with the antisymmetric and symmetric vibrations of a bridging acetate. It was not possible to identify bands associated with terminally bound carboxylates. In chloroform solution four carboxylate bands can be picked out. Bands at 1575 and 1380 cm^{-1} are associated with bridging carboxylate while the band at 1360 cm^{-1} is assigned to the symmetric stretch of a terminal carboxylate. The band at 1700 cm^{-1}, which is absent in the mull spectrum, must be due to the "missing" antisymmetric stretch of a terminally bound carboxylate.

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As with $Cu_2PAP(CH_3COO)_3$ (13), a loose intermolecular association is proposed between two terminal carboxylates on one binuclear complex with copper atoms on a neighbouring complex leading to a reduction in the antisymmetric frequency of the terminal carboxyl groups. This band is presumably hidden among the CN vibrations associated with the ligand itself in the solid state spectrum. The proposed intermolecular association would lead to a five-coordinate structure in the solid state (Fig. 5) but in solution, where the intermolecular association is broken, a four-coordinate system should exist. The observation of a *d–d* band in methanol at 17200 cm^{-1} is certainly consistent with a four-coordinate system in which the stereochemistry at the copper centres is distorted square planar.

The binuclear nitrate complex (**XXIV**) is obtained from the reaction between copper nitrate and PAP6Me in aqueous ethanol. An infrared absorption at 3480 cm^{-1} can be associated with a hydroxide bridge while nitrate combination bands are indicative of two types of nitrate (30). The absorption at 1750 cm^{-1} indicates an ionic nitrate while absorptions at 1724 and 1757 cm^{-1} suggest the presence of bidentate nitrate. The absence of a high energy nitrate combination band, indicative of the presence of a nitrate bridge, suggests a different structure for this complex than was observed for **XVI**. The *d–d* absorption in the solid state at 16400 cm^{-1} can be associated with five-coordinate copper(II) and a five-coordinate binuclear structure is suggested in the solid state involving a hydroxy bridge and two bidentate nitrate groups (Fig. 6). The low magnetic moment of 1.20 BM suggests significant exchange and supports the proposed double bridged structure. In aqueous solution a much lower energy *d–d* absorption is observed, suggesting the formation of a solvated derivative.

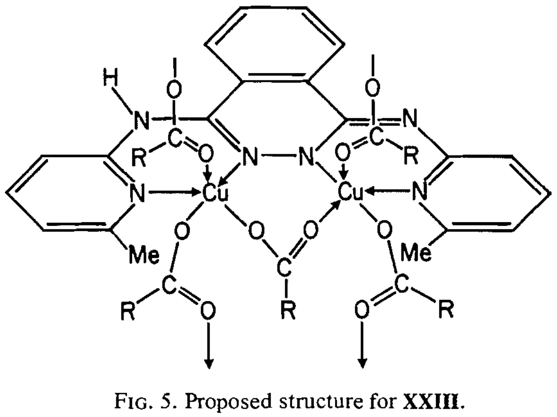

FIG. 5. Proposed structure for **XXIII**.

In the reaction between copper perchlorate and PAP6Me in aqueous ethanol two products are formed. Initially a yellow solid (**XXV**) is obtained followed by a green product (**XXVI**) on reduction of the volume of the mother liquor. **XXV** exhibits five infrared bands associated with CN stretch in the ligand and indicates the presence of protonated PAP6Me. This compound contains no metal and appears to be a diperchlorate salt in which the ligand is protonated at two sites (presumably both pyridine nitrogen atoms) (19). The formation of a salt of this type is a departure from the trend we have seen with the other systems in which, when the ligand acted as a base, mononuclear protonated complexes were formed. In the case of PAP6Me, however, the 6-methyl groups on the pyridine rings may exert enough of a steric influence that to form a mononuclear bis-bidentate ligand complex is not possible. Models suggest that this is so.

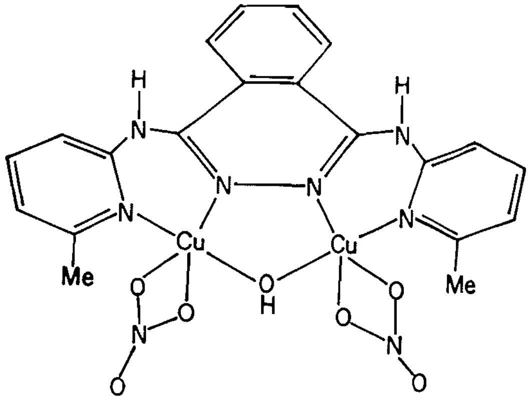

FIG. 6. Proposed structure for **XXIV**.

The green copper perchlorate complex (**XXVI**) is a binuclear derivative involving a hydroxide bridge and coordinated water. There is little evidence to suggest the involvement of perchlorate in the copper coordination sphere unless the slight splitting of the v_3 vibration is considered to be significant. In a recent paper Lippard and co-workers report the structure of a binuclear copper perchlorate complex of a binucleating macrocyclic ligand (35). In addition to a hydroxide bridge, a weakly bound bridging bidentate perchlorate group was also found to be present (Cu—O(perchlorate) ~ 2.6 Å). However, no infrared data were reported for the perchlorate group in this complex. Perhaps a rather weak splitting of v_3 would be expected in this case. The *d–d* absorption at 16700 cm^{-1} (**XXVI**) is consistent with a four-coordinate system involving one coordinated water molecule per copper centre and a hydroxide bridge (Fig. 6; NO_3 replaced by H_2O) but the possibility of a five-coordinate derivative should not be ruled out.

Binuclear copper complexes involving antifer-

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romagnetic exchange between metal centres are potential models for the binuclear oxygen-breathing protein hemocyanin and copper-containing oxidase enzymes, e.g. tyrosinase, laccase. Magnetic measurements on protein extracts indicate strong antiferromagnetic exchange between the copper(II) centres in Rhus vernicifera laccase ($-2J \geq 1000$ cm^{-1}) (36) and in oxyhemocyanin (Megathura crenulata; $-2J \geq 1250$ cm^{-1}) (37). Strong antiferromagnetic exchange is observed in binuclear copper systems involving single hydroxy bridges (29, 35, 38) and exchange increases with bridge angle (29, 34). An oxygen bridge from, e.g., tyrosine has been suggested as a super-exchange medium for both oxyhemocyanin (39) and enzymes containing Type III copper centres (35, 38) and other donor groups around the copper centres are thought to include histidine (38). With these properties in mind we see our complexes as potential models for such centres and are embarked on a program to investigate detailed magnetic and structural characteristics of some of our systems. We anticipate that varying the bridge groups between the copper centres and creating steric factors on the coordinated pyridine groups will alter the dimensions of the binuclear centre and vary the magnetic exchange.

The catecholase activity of the complex $[\mathrm{Cu}_2(\mathrm{PAP})(\mathrm{OH})\mathrm{Cl}_3]$ has already been demonstrated (20). Preliminary results indicate that this system also catalytically oxidizes ascorbic acid and that the complex $[\mathrm{Cu}_2(\mathrm{PAP6Me})(\mathrm{OH})\mathrm{Cl}_3]$ is also catecholase active. Reports on these studies will be published elsewhere.

Acknowledgement

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