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Binuclear Copper(I) Complexes of Some Tetradentate Pyridyl Phthalazines

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Binuclear copper(I) complexes of a series of pyridyl phthalazines have been prepared by the reaction of copper(I) salts with the ligands in acetonitrile. The two copper(I) centres are bound to the tetradentate ligands in dimeric or polymeric structures. The complexes are diamagnetic and oxygen sensitive, especially in solution. A binuclear copper(I) complex has been isolated from the ascorbic acid reduced aqueous solution of $[Cu_2(PAP)(OH)Cl_3]$*, (PAP = 1,4-di(2'-pyridyl)aminophthalazine) which does not contain coordinated ascorbic acid. However aerial oxidation of the ascorbic acid reduced aqueous solution of the same complex produces a binuclear copper(II) species containing one molecule of ascorbate. Aerial oxidation of a dimethylsulfoxide solution of a binuclear copper(I) complex produces a binuclear hydroxy bridged copper(II) species.*

Introduction

Binuclear copper complexes in which the two metal centres are brought into close proximity are of considerable interest because the biological function of many metalloproteins is believed to be associated with the occurrence of pairs of adjacent metal ions capable of mutual interaction via small bridging groups. In certain oxidase and oxygenase enzymes binuclear copper(II) centres (Type III centres) are found which are EPR non detectable and in which the two metal ions are strongly antiferromagnetically coupled [1, 2]. The Type III copper centres appear to function as two electron acceptor sites and are thought to be the site of interaction with dioxygen [1, 2]. In the oxygen-carrying hemocyanins oxygen uptake is assumed to occur at a colourless binuclear copper(I) site with the formation, in an equilibrium process, of a blue binuclear peroxide bridged copper(II) centre [3].

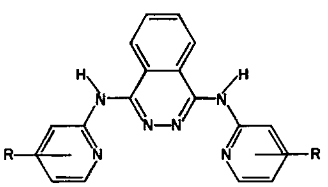

Fig. 1. PAP (R = H), PAP3Me (R = 3 methyl), PAP5Me (R = 5 methyl), PAP6Me (R = 6 methyl).

In recent studies involving potentially tetradentate binucleating pyridyl phthalazine ligands (Fig. 1) we have described numerous binuclear hydroxy bridged copper(II) complexes in which the metal centres are antiferromagnetically coupled. X-ray structures have revealed binuclear systems involving copper–copper separations in the range 3.0–3.2 Å with Cu–O–Cu bridge angles in the range 100–115° and magnetic studies have shown exchange couplings up to $-2J = 520$ cm^{-1} [4–9]. The metal–metal separation and hence Cu–O–Cu bridge angle in systems of this sort can be varied by inserting non-hydroxy groups of various sizes between the metal centres, thus tuning the dimensions of the binuclear centre.

In addition to having structural features at their binuclear centres thought to be typical of the binuclear copper proteins themselves a number of binuclear copper pyridyl phthalazine complexes have been shown to exhibit oxidase activity. $[Cu(PAP)(OH)Cl_3]\cdot 1.5H_2O$ and $[Cu_2(PAP)(OAc)_3]$ (PAP = 1,4-di(2'-pyridyl)aminophthalazine; Fig. 1) catalytically oxidize excess catechol in the presence of oxygen in aqueous acetonitrile [10] and also appear to exhibit phenolase activity [10]. The related complex $[Cu_2(PAP6Me)(OH)Cl_3]$ also exhibits catecholase activity [9].

In mimicking catecholase action binuclear copper(I) species are implicated as intermediates. Such species can be identified spectroscopically by changes in key charge transfer absorptions associated with both the ligand, PAP, and the catechol and its quinone form [10]. Isolation of such species has so far been limited to one report in which the complex $[Cu_2PAP]ClO_4$ was obtained by addition of excess perchlorate to the aqueous solution resulting from the addition of hydrazine to aqueous $[Cu_2(PAP)(OH)Cl_3]\cdot 1.5H_2O$ [11].

In this report we describe the synthesis and characterization of some binuclear copper(I) complexes of

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the ligands PAP, PAP3Me (1,4-di(3′-methyl-2′-pyridyl)aminophthalazine, PAP5Me (1,4-di(5′-methyl-2′-pyridyl)aminophthalazine) and PAP6Me (1,4-di(6′-methyl-2′-pyridyl)aminophthalazine (Fig. 1) using acetonitrile as solvent. Some preliminary details of the ascorbate oxidase activity of the complex $[Cu_2(PAP)(OH)Cl_3]\cdot1.5H_2O$ will also be described.

Experimental

The ligands PAP, PAP3Me, PAP5Me and PAP6Me were synthesized as described previously [4, 6, 8].

$[Cu(PAP)]_nCl_n$ (I)

PAP (1.0 g; 3.2 mmol) was dissolved in refluxing degassed acetonitrile (200 ml). CuCl (0.32 g; 3.2 mmol) was dissolved in degassed acetonitrile (75 ml) and the cold solution of cuprous chloride added to the refluxing PAP solution under nitrogen. Immediately a deep red-brown coloured solution formed from which an orange-brown solid precipitated after a few minutes. The mixture was refluxed for 1 h under nitrogen and the product filtered in air, washed with acetonitrile and dried *in vacuo* at room temperature (yield 1.3 g).

$[Cu(PAP)_n]Br_n$ (II), $[Cu(PAP)Br]_2(CH_3CN)_2$ (III)

PAP (1.0 g; 3.2 mmol) was dissolved in refluxing degassed acetonitrile (200 ml). CuBr (0.46 g; 3.2 mmol) was dissolved in degassed acetonitrile (75 ml) and added to the refluxing PAP solution under nitrogen. An intense red-brown colouration was observed and after refluxing for 15–20 m a red-brown solid began to form. The mixture was refluxed under nitrogen for 1½ h and the product (II) filtered off, washed with acetonitrile and dried *in vacuo* at room temperature (yield 0.75 g).

The mother liquor was allowed to stand overnight with the formation of dark red-brown irregularly shaped crystals. This product (III) was filtered off, washed with acetonitrile and dried *in vacuo* at room temperature (yield 0.70 g).

$[Cu_2(PAP)Br_2]_2$ (IV)

PAP (0.5 g; 1.6 mmol) was dissolved in refluxing degassed acetonitrile (100 ml). CuBr (0.47 g; 3.3 mmol) was dissolved in acetonitrile (50 ml) and added to the refluxing PAP solution under nitrogen. Initially a deep red-brown coloured solution formed followed by a dirty brown precipitate. The solid subsequently dissolved and after 10 m red-brown crystals formed. Refluxing was continued for 45 m and the mixture cooled to room temperature. The product was filtered, washed with acetonitrile and dried *in vacuo* at room temperature (yield 0.85 g).

$[Cu(PAP)]_n(NO_3)_nnH_2O$ (V)

$Cu(NO_3)_2\cdot3H_2O$ (1.0 g; 4.1 mmol) was dissolved in deoxygenated acetonitrile (100 ml) under nitrogen. Copper powder (1.0 g; 16 mmol) was added and the mixture stirred under nitrogen until the solution became colourless. The solution was filtered from excess copper, PAP (0.65 g; 2.1 mmol) added and the mixture stirred under nitrogen at room temperature for several hours. A brown precipitate formed which was filtered under nitrogen, washed with degassed acetonitrile and dried under vacuum.

The other copper(I) complexes (VI–IX, XI–XVI) were prepared in a similar fashion except that in some cases, where the added ligand did not dissolve completely on stirring at room temperature, the reaction mixture was refluxed for several hours. The products were obtained as orange or brown solids.

$[Cu_2(PAP)(OH)_2(H_2O)(ClO_4)]ClO_4\cdot0.5H_2O$ (XVII)

A sample of $[Cu_2(PAP)Br_2]_2$ was dissolved in a minimal volume of DMSO and the brown solution stirred at room temperature in air for 6 h. The resulting green solution was then added to a saturated aqueous solution of sodium perchlorate whereupon, on standing, green crystals formed. The product was filtered, washed quickly with water and dried under vacuum at 70 °C for 3 h.

All the copper(I) complexes were found to be diamagnetic when freshly prepared. In general these systems have low solubility in organic solvents and are air sensitive in solution. Molecular weight determinations were therefore not attempted.

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 Suceptibility system, coupled to a Cahn gram electrobalance. 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

Addition of aqueous hydrazine hydrate to a solution of the binuclear copper(II) complex $[Cu_2(PAP)(OH)Cl_3]\cdot1.5H_2O$ in a mixture of acetonitrile and water causes reduction to copper(I) with a change in colour from green to reddish-brown. A shift in the $\pi-\pi^*$ charge transfer band from 29400 cm^{-1} to 25500 cm^{-1} is also observed indicating that the neutral ligand, present in the copper(II) complex, forms an anion by proton loss on reduction [4]. The reduced species can be reoxidized in the presence of molecular oxygen to the initial copper(II) complex and the redox process repeated over several cycles [10]. It is assumed that the binuclear integrity of the complex is maintained on reduction, a feature which is also implied by the proposed mechanism of the catecholase cycle of this and other species [10].

Electronic spectra of aqueous solutions of species of the type $[Cu_2(PAP)(OH)X_3]$ (X = Cl, Br, OAc, IO_3 etc) are almost identical, suggesting that the same solvated species is present in all cases. Therefore, the reduction of such systems in aqueous solution using, *e.g.* hydrazine, would presumably produce the same copper(I) species. Consequently, in this study, a direct synthetic approach to a variety of copper(I) derivatives of PAP and related ligands (Fig. 1) was employed using copper(I) salts in acetonitrile.

In general the copper(I) complexes obtained by a direct synthetic route in acetonitrile are dark coloured, ranging from orange to dark brown, and have very limited solubility in acetonitrile. Many are very air sensitive in solution, giving green copper(II) products on exposure to air, and some have air sensitivity even in the solid state. All the complexes reported are diamagnetic when freshly prepared implying the presence of copper(I) centres, but in those cases where air sensitivity exists non-zero magnetic moments were obtained on prolonged exposure of the sample to air.

Compounds I and II have very similar infrared and charge transfer spectra and no far infrared bands are observed which can be associated with terminal or bridging copper–halogen bonds. The presence of a π–π^* charge transfer absorption above 26000 cm^{-1} has been used in the past to indicate the presence of neutral PAP [4] while the observation of a single band below 26000 cm^{-1} implies anionic ligand. Neutral ligand is therefore present in both cases. Both compounds exhibit pyridine ring breathing mode vibrations above 1000 cm^{-1}, indicative of coordination of the pyridine rings [4], suggesting that the ligand (PAP) behaves in a tetradentate fashion. A reasonable structure for these compounds would involve two four coordinate metal centres sandwiched between two adjacent neutral ligands, which could exist in a polymeric or dimeric arrangement, the halogens, existing as anionic groups.

Compounds II and III were prepared in the same reaction involving a 1:1 (ligand:metal) stoichiometry in acetonitrile. It was obtained as an insoluble red-brown solid, formed during the reaction, while III was obtained as a crystalline solid from the mother liquor. Compound III has a low energy change transfer absorption at 23300 cm^{-1} (Table I) with a shoulder at 29400 cm^{-1} implying the presence of neutral ligand [4]. The low energy change transfer absorption may be associated with bound bromine rather than PAP$^{\cdot}$. Pyridine ring breathing absorption indicates coordinated pyridine rings (Table II) and a tetradentate ligand and an absorption at 253 cm^{-1} suggests the presence of terminal Cu–Br bonds. Other absorptions at 2253 cm^{-1} and 2293 cm^{-1} indicate the presence of lattice bound acetonitrile [12]. This

TABLE I. Analytical Data.

	Compound	Found (%)				Calcd (%)			
		C	H	N	Cu	C	H	N	Cu
I	$[Cu(PAP)]_nCl_n$	52.3	3.31	20.2	14.9	52.3	3.39	20.3	15.4
II	$[Cu(PAP)]_nBr_n$	46.9	3.05	18.4	13.6	47.2	3.06	18.4	13.9
III	$[Cu(PAP)Br]_2(CH_3CN)_2$	47.5	3.41	19.2	12.8	48.1	3.41	19.7	12.7
IV	$[Cu_2(PAP)Br_2]_2$	35.7	2.35	13.9	20.7	35.9	2.33	14.0	21.1
V	$[Cu(PAP)]_n(NO_3)_n \cdot nH_2O$	47.5	3.12	21.0	13.7	47.2	3.50	21.4	13.9
VI	$[Cu(PAP)]_n(ClO_4)_n \cdot 0.5nH_2O$	44.6	2.91	16.9	13.3	44.4	3.09	17.3	12.8
VII	$[Cu_2(PAP3Me)Cl_2]_2$	44.7	3.32	15.4	23.4	44.4	3.33	15.5	23.5
VIII	$[Cu_2(PAP3Me)Br_2]_2$	38.8	2.71	13.5	20.5	38.2	2.86	13.4	20.2
IX	$[Cu(PAP3Me)]_n(ClO_4)_n \cdot 0.5nCH_3CN$	47.4	3.60	17.0	12.0	47.9	3.71	17.3	12.1
X	$(Cu_3(PAP5Me)(OH)_4Cl_2] \cdot 0.5EtOH$	36.1	3.01	12.1	26.7	36.3	3.60	12.1	27.4
XI	$[Cu(PAP5Me)]_n(NO_3)_n \cdot nH_2O$	49.3	3.89	19.9	13.1	49.4	4.12	20.2	13.1
XII	$[Cu(PAP5Me)]_n(ClO_4)_n \cdot 2nH_2O$	44.1	3.46	15.8	11.5	44.4	4.07	15.5	11.7
XIII	$[Cu_2(PAP6Me)Cl_2] \cdot H_2O$	43.3	3.20	14.9	23.0	43.0	3.58	15.0	22.8
XIV	$[Cu_2(PAP6Me)Br_2]$	38.4	2.93	13.5	19.9	38.2	2.86	13.4	20.2
XV	$[Cu(PAP6Me)]_n(NO_3)_n \cdot 0.5nH_2O$	50.2	4.05	20.5	13.1	50.4	3.98	20.6	13.3
XVI	$[Cu(PAP6Me)]_n(ClO_4)_n \cdot nCH_3CN \cdot 0.5nH_2O$	47.8	3.60	17.3	11.5	47.6	3.96	17.7	11.4
XVII	$[Cu_2(PAP)(OH)_2(H_2O)(ClO_4)] \cdot ClO_4 \cdot 0.5H_2O$	30.9	2.34	11.8	17.9	30.8	2.71	12.0	18.1

TABLE II. Electronic (Mull Tansmittance) and Infrared Spectra.

	Compound	CT (cm^{-1})	Infrared (cm^{-1})
I	$[Cu(PAP)]_nCl_n$	[23500] 28600	1002, 1006 (pyr)
II	$[Cu(PAP)]_nBr_n$	[23800] 29400	1001, 1011 (pyr)
III	$[Cu(PAP)Br]_2(CH_3CN)_2$	23300 [29400]	1008 (pyr), 253 (Cu–Br) 2253, 2293 (CH_3CN)
IV	$[Cu_2(PAP)Br_2]_2$	23300 [28600]	1007 (pyr)
V	$[Cu(PAP)]_n(NO_3)_n \cdot nH_2O$	[23300] [28600]	1008 (pyr), 1330 (NO_3^-) 1747 ($\nu_1 + \nu_4$, NO_3^-)
VI	$[Cu(PAP)]_n(ClO_4)_n \cdot 0.5nH_2O$	[24400] [29400]	1002 (pyr), 1080 (ClO_4^-) 3580 (H_2O)
VII	$[Cu_2(PAP3Me)Cl_2]_2$	24700	272 (Cu–Cl)
VIII	$[Cu_2(PAP3Me)Br_2]_2$	25600	
IX	$[Cu(PAP3Me)]_n(ClO_4)_n \cdot 0.5nCH_3CN$	23500	1100 (ClO_4^-), 2240, 2280 (CH_3CN)
X	$(Cu_3(PAP5Me)(OH)_4Cl_2] \cdot 0.5EtOH$	28600, 15200 [13300], [11800]	260, 280, 290 sh (Cu–Cl) 3620 (OH)
XI	$[Cu(PAP5Me)]_n(NO_3)_n \cdot nH_2O$	26700	1330 (NO_3^-), 1746 ($\nu_1 + \nu_4$, NO_3^-)
XII	$[Cu(PAP5Me)]_n(ClO_4)_n \cdot 2nH_2O$	27800	1100 (ClO_4^-), 3560 (H_2O)
XIII	$[Cu_2(PAP6Me)Cl_2] \cdot H_2O$	25000	305 (Cu–Cl)
XIV	$[Cu_2(PAP6Me)Br_2]$	25000	252 (Cu–Br)
XV	$[Cu(PAP6Me)]_n(NO_3)_n \cdot 0.5nH_2O$	28600	1755 ($\nu_1 + \nu_4$, NO_3^-) 3520, 3580 (H_2O)
XVI	$[Cu_2(PAP)(OH)_2(H_2O)(ClO_4)]ClO_4 \cdot 0.5H_2O$	[24400]	1060 (ClO_4^-), 2242, 2292 (CH_3CN)
XVII	$[Cu_2(PAP)(OH)_2(H_2O)(ClO_4)]JClO_4J0.5H_2O$	28600 [25000] 16700 (d–d)	3630, 3645, 3660 (OH), 3465 (H_2O), 1130 sh, 1100, 1060 sh (ClO_4^-), 1020 (pyr)

compound can be assigned a simple dimeric structure involving two five-coordinate copper(I) centres sandwiched between two adjacent ligands (Fig. 2).

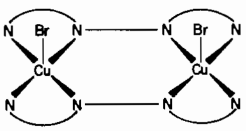

Fig. 2. Proposed structure for III.

Compound IV was obtained as the only product from acetonitrile using a 1:2 (ligand:metal) ratio. Again a high energy charge transfer band is observed indicating the presence of neutral ligand, which appears to be tetradentate. No infrared absorption associated with terminal Cu–Br bonds was observed and bromine bridges seem likely. Structurally IV appears to be analogous to some 2-pyridinealdazine complexes of copper(I), $Cu_2(PAA)X_2$ (X = Cl, Br) reported by Stratton and Busch [13]. For these systems a dimeric structure was proposed involving pairs of copper(I) centres bound between two adjacent ligands and bridged by halogen atoms. A similar arrangement is shown in Fig. 3 to represent IV. The low solubility of this system may however indicate a more polymeric arrangement based on this simple structure.

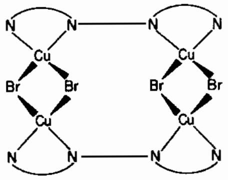

Fig. 3. Proposed structure for IV.

Compounds V and VI clearly contain tetradentate ligand and the anionic groups are uncoordinated (Table II). The general similarity in the infrared spectra of these systems with those of I and II suggests a similar structure. The charge transfer region of the electronic spectra of V and VI exhibits two bands in each case with one absorption above 26000 cm^{-1} indicating the presence of neutral ligand.

No definitive infrared bands have been found that would allow unequivocal assignment of the denticity of the ligands other than PAP [4] (a pyridine ring breathing vibration cannot be picked out in the methyl substituted ligands). However it is assumed that PAP3Me, PAP5Me and PAP6Me behave as tetradentate ligands in a similar fashion to PAP itself. Also, while it was possible to use charge transfer absorptions in most cases to indicate the charged state of the ligand PAP, similar assignments could not be made for the methylated derivatives bound to copper(I) centres. However analytical data indicate that in these, and other cases, the ligands are neutral.

The infrared spectra of VII and VIII are almost superimposable, with the exception of a band at 272 cm^{-1} in the chloro-complex which is absent in the bromide. This band can possibly be assigned to bridging copper–chlorine bonds. Structurally VII and VIII appear to be similar to IV (Fig. 3) and may exist as a dimer or a polymer.

Compound IX has an ionic perchlorate according to infrared studies (Table II) and also lattice bound acetonitrile and appears to have a structure similar to that of compounds I and II in which the copper(I) centre is four coordinate.

The chloro-complex of PAP5Me is obtained as an air sensitive, diamagnetic orange powder which forms a green solid on prolonged exposure to air. Poor analytical data were obtained for the orange copper(I) species due to its air sensitivity, and so it is not reported. The green oxidized product was extracted into hot DMF and a green solid obtained on cooling, which was recrystallized from ethanol (X). This complex has an unusual microanalysis suggesting more than two copper centres per molecule. A reasonable empirical formula involves three copper atoms, four hydroxide groups, presumably bridging entities, and two chlorides. d–d absorptions in the range 11800–15200 cm^{-1} indicate the presence of copper(II) ions and a low magnetic moment (1.41 BM per copper) indicates an exchange coupled species involving single atom bridges between the copper(II) centres. Hydroxy bridges seem reasonable because of their propensity for exchange [6, 8 and references therein] and the fact that a sharp infrared absorption is observed at 3620 cm^{-1}. The presence of Cu–Cl bonds is indicated by far infrared absorption in the range 260–290 cm^{-1} (Table II). The formation of a hydroxy bridged polynuclear species on reaction with oxygen seems eminently reasonable in the light of the oxidizing action of molecular oxygen in the presence of water ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, $\epsilon^0 = 0.401$ V).

The PAP5Me complexes of copper nitrate and perchlorate (XI, XII) both contain ionic anionic groups (Table II) and in general have very similar infrared spectra suggesting the same structure which is likely to be similar to that suggested for I and II involving either a dimeric or polymeric arrangement. The same structural situation probably exists for XV and XVI, involving PAP6Me and copper nitrate and perchlorate respectively. Ionic anions are indicated and the infrared spectra of the two compounds are in general very similar.

The copper chloride and bromide complexes of PAP6Me (XIII, XIV) have almost identical infrared spectra in the region above 600 cm^{-1}. In the far infrared a band at 305 cm^{-1} for the chloride, absent in the bromide, suggests the presence of terminal copper–chlorine bonds. Also a band at 252 cm^{-1} in the bromide, absent in the chloro-complex, implies the presence of terminal copper–bromine bonds. Structurally, therefore, XV and XVI do not resemble the other binuclear halide derivatives (Fig. 3). Since no evidence exists for bridging halogen bonds a binuclear three-coordinate structure is suggested involving tetradentate PAP6Me and one terminal halogen per copper centre. The presence of methyl groups on the six-position of the pyridine rings may reasonably present enough of a steric constraint that the formation of a dimeric structure (Fig. 3) is not possible. Some major structural differences between copper(II) complexes of PAP6Me and PAP4, 6DiMe and other pyridyl phthalazine systems, with no such substituents, have already been observed [6, 8].

The reversible redox behaviour of species like $[Cu_2(PAP)(OH)X_3]$ (X = Cl, Br) in aqueous solution has already been demonstrated using hydrazine as the reducing agent [9]. It seems reasonable to assume therefore that a species like IV, which is a binuclear entity analogous to *e.g.* $[Cu_2(PAP)(OH)Br_3]$, would react with molecular oxygen in solution to produce a binuclear copper(II) complex. Compound IV was dissolved in degassed DMSO in an anerobic cell assembly and its electronic spectrum run in the absence and presence of molecular oxygen. In degassed DMSO IV exhibits a weak band at 13600 cm^{-1}, which may be associated with a trace amount of copper(II) impurity in the solution. On flushing the cell with oxygen and stirring the solution a rather slow reaction occurred resulting ultimately in the formation of a green solution. After four hours the spectrum showed just one fairly intense band at 16500 cm^{-1}. For comparison a DMSO solution of the complex $[Cu_2(PAP)(OH)Br_3]$ showed one major absorption at 16000 cm^{-1} probably due to a solvated species of the type $[Cu_2(PAP)(OH)(DMSO)_4]Br_3$ [4].

The perchlorate complex XVII was obtained as a green solid from an aerially oxidized DMSO solution of IV. Infrared data clearly indicate the presence of hydroxy groups and water and the presence of a band at 1020 cm^{-1} confirms the binuclear nature of the complex [4]. The rather broad perchlorate absorption with three discernable components suggests the presence of an ionic perchlorate and the possibility of a weakly bound monodentate perchlorate. The magnetic moment of this complex (1.9 BM per copper centre at room temperature) confirms the presence of copper(II) and the probable absence of antiferromagnetic exchange between metal centres, a feature observed for many monohydroxy bridged binuclear copper(II) complexes of PAP and related ligands [4, 6, 8]. XVII appears to be a dihydroxy bridged species, probably involving five-coordinate copper(II) centres, with the fifth coordination sites being occupied by water at one copper centre and monodentate perchlorate at the other. The high room temperature magnetic moment is typical of some dihydroxy bridged binuclear copper(II) systems which exhibit ferromagnetic rather than antiferromagnetic exchange between the metal centres [14]. A d–d absorption in the mull transmittance spectrum at 16700 cm^{-1} is almost identical to that observed for the oxidized solution of IV in DMSO indicating the formation of a similar species in both cases.

Aqueous solutions of ascorbic acid have been widely used as a reducing medium by inorganic chemists [15–19] and it is no surprise to find that addition of one equivalent of ascorbic acid to an aqueous acetonitrile solution of $[Cu_2(PAP)(OH)Cl_3]$ causes an immediate colour change from green to red-brown. Addition of excess perchlorate to this solution precipitates an air sensitive brown coloured solid which analyzes $Cu_2(PAP)(ClO_4)_2 \cdot (CH_3CN)_3 \cdot 2H_2O$. The complex is diamagnetic, implying the presence of copper(I), is binuclear according to infrared studies but contains no ascorbate residue. On exposure of an aqueous solution of $[Cu_2(PAP)(OH)Cl_3] \cdot 1.5H_2O$, reduced with one equivalent of ascorbic acid, to air for several days a green solution formed from which, on reduction in volume, green crystals were obtained. This compound analyses as $[Cu_2(PAP)(OH)Cl_3(C_6H_5O_6)] \cdot 6H_2O$, has a magnetic moment $\mu = 1.7$ BM, infrared bands indicative of the presence of ascorbic acid and a d–d absorption (mull transmittance) at 15400 cm^{-1} consistent with a five-coordinate derivative. Also preliminary studies indicate that the oxidation of excess ascorbic acid in air is catalyzed by $[Cu_2(PAP)(OH)Cl_3]$ and related systems. More complete details of this study will be published elsewhere.

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