

Binuclear Copper(II) Complexes of the Ligand 1,4-Di-(2'-pyridyl)aminophthalazine

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Abstract

Reaction of the binuclear complex $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ (PAP = 1,4-di-(2'-pyridyl)aminophthalazine), which has a hydroxide bridge, a chloride bridge and a diazine (N-N) bridge, with various anions in water and buffered (pH 6.86) solutions leads mainly to the formation of spin coupled complexes with room temperature magnetic moments <1.5 B.M. Most of these complexes retain the hydroxide bridge, in addition to the diazine bridge, and in several systems only two bridge groups exist. Very low magnetic moments ($\mu < 1.2$ B.M.) are observed for these double bridged complexes, comparable with values observed for triple bridged systems involving large bridging, polyatomic anions. In certain cases prevailing pH conditions are sufficiently basic that ligand deprotonation occurs. Deprotonated complexes are also produced by reaction of $[\text{Cu}_2(\text{PAP}-\text{H})(\text{CH}_3\text{COO})_3]$ (PAP - H = deprotonated ligand) with certain anions. Magnetic data have been used to project the possible dimensions of the binuclear centres in several μ -hydroxo bridged complexes, based on a linear relationship between μ (RT) and Cu-O-Cu angle observed elsewhere for related complexes.

Introduction

Binuclear hydroxide bridged copper(II) complexes involving antiferromagnetic exchange between the metal centres are potential models for the active sites in certain binuclear copper proteins. Strong antiferromagnetic coupling is observed between the copper(II) centres in *Rhus vernicifera* laccase [1] ($-2J \geq 1000 \text{ cm}^{-1}$) and in oxyhemocyanin (*Megathura crenulata*; $-2J \geq 1250 \text{ cm}^{-1}$) [1, 2]. Strong antiferromagnetic exchange is also observed in binuclear copper(II) systems involving single hydroxide

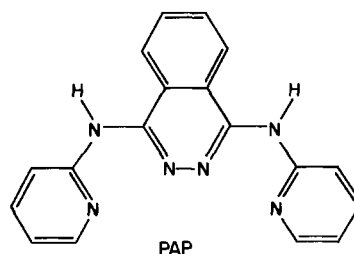


Fig. 1. PAP, 1,4-di-(2'-pyridyl)aminophthalazine.

bridges [3-8] and exchange in general increases with increasing oxygen bridge angle.

In a series of binuclear copper(II) complexes involving tetradentate aminophthalazine ligands and six-membered chelate rings, in which the metal centres are bridged by a diazine entity ($=\text{N}-\text{N}=\text{}$), a hydroxide and a bridging anion, it has been shown that the dimensions of the binuclear centre and especially the oxygen bridge angle and metal-metal separation, can be varied according to the size and 'bite' of the anion bridge [6, 7]. As the oxygen bridge angle and copper-copper separation are increased stronger antiferromagnetic exchange is observed. An exchange integral of about 200 cm^{-1} ($-2J$) was observed for a bridge angle of about 100 deg ., increasing to an exchange of about 500 cm^{-1} for an angle of 115 deg . In another system involving just a diazine and a hydroxide bridge and five-membered chelate rings, an oxygen bridge angle of 126 deg . was observed with an exchange of 800 cm^{-1} [7].

In an attempt to extend this concept of 'tuning' the dimensions of the binuclear centre in copper phthalazine complexes we have examined the role of a variety of other anionic groups (e.g. NO_2^- , NCS^- , N_3^- , ClO_4^- , $\text{C}_2\text{O}_4^{2-}$, CNO^- , PO_4^{3-}) as potentially bridging entities by reacting $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{PAP}-\text{H})(\text{CH}_3\text{COO})_3]$ (PAP = 1,4-di-(2'-pyridyl)aminophthalazine Fig. 1) dissolved in water or a phosphate buffer solution, with the appropriate anion. In most cases the hydroxide bridge is retained, as is indicated by reduced magnetic

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TABLE I. Analytical and Other Data.

Compound	Colour	Found (%)				Calcd (%)			
		C	H	N	Cu	C	H	N	Cu
I [Cu ₂ (PAP - H)(OH)(NO ₂) ₂] · 4H ₂ O	Green	34.7	2.88	18.4	20.1	34.8	3.38	18.0	20.5
II [Cu ₂ (PAP)(OH)(NCS) ₃]	Green	40.2	2.16	19.7	19.5	39.9	2.37	19.9	20.1
III [Cu ₂ (PAP - H)(N ₃) ₃] · H ₂ O	Khaki	37.5	2.00	36.1	21.1	37.0	2.57	36.0	21.7
IV [Cu ₂ (PAP)(OH)Cl ₂]ClO ₄ · 5H ₂ O	Khaki-green	34.1	2.69	12.9		33.9	2.51	13.2	
V [Cu ₂ (PAP - H)Cl ₂ (H ₂ O)]ClO ₄	Green	33.4	2.50	12.7	19.1	33.4	2.63	12.9	20.2
VI [Cu ₂ (PAP)(C ₂ O ₄) ₂]	Green	43.0	2.25	14.0		42.8	2.27	13.6	
VII [Cu ₂ (PAP - H)(OH)(HPO ₄)] · 1.5H ₂ O	Brown	37.4	2.76	14.5	21.8	37.2	3.10	14.5	21.9
VIII [Cu ₂ (PAP - H)(OH)(CNO) ₂]	Green	44.1	2.34	20.4	23.2	44.3	2.58	20.7	23.5
IX [Cu ₂ (PAP - H)(SO ₄) _{1.5} (H ₂ O)]	Green	35.9	2.75	13.7	20.8	35.9	2.49	13.9	21.1
X [Cu ₂ (PAP)(OH)(SO ₄) _{1.5} (H ₂ O)]	Green	35.0	2.52	13.8	20.1	34.8	2.74	13.5	20.5
XI [Cu ₂ (PAP - H)(OH) ₂ (H ₂ O)(ClO ₄)] · 0.5H ₂ O	Khaki-green	35.9	2.44	13.7		36.0	2.99	14.0	
XII [Cu ₂ (PAP)(OH)(CH ₃ COO)Cl ₂] ^a	Turquoise	40.7	2.96	14.2		40.9	3.07	14.3	
XIII [Cu ₂ (PAP)(OH)(C ₅ HN ₂ O ₄)(H ₂ O) ₂] · 7H ₂ O	Blue	35.7	3.60	14.4	16.4	35.7	4.40	14.5	16.4
XIV [Cu ₂ (PAP)(OH)(C ₅ HN ₂ O ₄)] · 7H ₂ O	Green	37.5	3.00	15.2	17.2	37.5	4.07	15.2	17.2

^aFound Cl 11.9%, Calcd. Cl 12.1%.

moments, and in some cases anion bridging is indicated by infrared data.

Experimental

The ligand PAP was prepared according to published procedures [9, 10].

[Cu₂(PAP)(OH)(NCS)₃] (II)

[Cu₂(PAP)(OH)Cl₃] · 1.5H₂O (9) (0.5 g, 0.85 mmol) was dissolved in hot water (100 ml) and excess solid sodium thiocyanate added. A lime green solid formed immediately, which was filtered, washed with water and dried at 80 °C *in vacuo* for 2 h. Compounds **I**, **III**, **IV** were prepared in a similar manner using a sodium salt of the appropriate anion. Compound **XIII** was prepared similarly by reaction of aqueous [Cu₂(PAP)(OH)Cl₃] · 1.5H₂O with an aqueous solution of one equivalent of 3,5-pyrazole dicarboxylic acid. **XIV** was produced by drying **XIII** *in vacuo* at 75 °C for several hours.

[Cu₂(PAP)(C₂O₄)₂] (VI)

[Cu₂(PAP)(OH)Cl₃] · 1.5H₂O (0.5 g, 0.85 mmol) was dissolved in pH 6.86 phosphate buffer (50 ml) and a saturated solution of K₂C₂O₄ added until a pale green precipitate formed. The product was filtered, washed with water and dried *in vacuo* at 80 °C for 2 h. Compounds **V**, **VI** and **VIII** were prepared similarly using appropriate anions.

[Cu₂(PAP - H)(SO₄)_{1.5}] · H₂O (IX)

Cu₂(PAP - H)(CH₃COO)₃ (9) (0.5 g, 0.81 mmol) was dissolved in hot water (75 ml) and excess solid Na₂-

SO₄ added. A light khaki-green precipitate formed which was filtered, washed with water and dried at 80 °C *in vacuo* for 2h. **XI** was prepared in a similar manner.

[Cu₂(PAP)(OH)(SO₄)_{1.5}] · 0.5H₂O (X)

CuSO₄ · 5H₂O (1.0 g, 4.0 mmol) was dissolved in hot water (100 ml), PAP (0.63 g, 2.0 mmol) added and the mixture refluxed until the ligand dissolved giving a bright green solution. The volume of the solution was reduced on a steam bath until green crystals formed. After standing overnight the product was filtered, washed with a minimal amount of ice water and dried *in vacuo* at 80 °C for 2 h.

[Cu₂(PAP)(OH)(CH₃COO)Cl₂] (XII)

[Cu₂(PAP)(OH)Cl₃] · 1.5H₂O (0.3 g; 0.5 mmol) was dissolved in 0.1 M ammonium acetate (40 ml) and the solution filtered. Turquoise crystals formed on standing at room temperature for several days, which were filtered with water and dried in air.

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. Microanalyses were carried out by Canadian Micro-analytical Service, Vancouver (C, H, N). Metal analyses were determined by atomic absorption with

TABLE II. Infrared Spectra.

Compound	Infrared (cm ⁻¹)
I [Cu ₂ (PAP – H)(OH)(NO ₂) ₂]·4H ₂ O	3640(OH ⁻), 3420(H ₂ O), 1360, 1035, 837(NO ₂ ⁻), 1014(pyr), 344(Cu–O)
II [Cu ₂ (PAP)(OH)(NCS) ₃]	3605(OH ⁻), 2080, 2063, 2040(NCS ⁻), 1024(pyr)
III [Cu ₂ (PAP – H)(N ₃) ₃]·H ₂ O	3550(H ₂ O), 2083, 2038, 2000, 1345, 1142, 720, 630(N ₃ ⁻), 1006(pyr)
IV [Cu ₂ (PAP)(OH)Cl ₂]ClO ₄ ·5H ₂ O	3600(OH ⁻), 1100(ClO ₄ ⁻), 1024(pyr), 282, 278(Cu–Cl)
V [Cu ₂ (PAP – H)Cl ₂ (H ₂ O)]ClO ₄	3540(H ₂ O), 1090(ClO ₄ ⁻), 1020(pyr), 290, 265(Cu–Cl)
VI [Cu ₂ (PAP)(C ₂ O ₄) ₂]	1670(ν _{as} C=O, C ₂ O ₄ ²⁻), 1010(pyr), 785(6 O–C=O), (C ₂ O ₄ ²⁻), 325, 300, 290(Cu–O)
VII [Cu ₂ (PAP – H)(OH)(HPO ₄)]·1.5H ₂ O	3610(OH ⁻), 3400(H ₂ O), 1075, 1060, 1046, 975, 965, 555, 534, 525(HPO ₄ ²⁻), 1012(pyr)
VIII [Cu ₂ (PAP – H)(OH)(CNO) ₂]	3580(OH ⁻), 3320(NH), 2240, 2210, (NCO ⁻), 1018 (pyr)
IX [Cu ₂ (PAP – H)(SO ₄) _{1.5} ·(H ₂ O)]	3400(H ₂ O), 1155, 1100, 1090, 1035, 1012, 970 (SO ₄ ²⁻)
X [Cu ₂ (PAP)(OH)(SO ₄) _{1.5} ·(H ₂ O)]	3640(OH ⁻), 1160, 1105sh, 1070, 1040sh, 1018, 980 (SO ₄ ²⁻)
XI [Cu ₂ (PAP – H)(OH) ₂ (H ₂ O)(ClO ₄)]·5H ₂ O	3540(OH ⁻), 3480(H ₂ O), 1130, 1070 (ClO ₄ ⁻)
XII [Cu ₂ (PAP)(OH)(CH ₃ COO)Cl ₂]	3640(OH ⁻), 1573, 1400(CH ₃ COO ⁻), 1020(pyr), 290, 308(Cu–Cl)
XIII [Cu ₂ (PAP)(OH)(C ₅ HN ₂ O ₄)(H ₂ O) ₂]·7H ₂ O	1650br,s (COO ⁻), 1012(pyr)
XIV [Cu ₂ (PAP)(OH)(C ₅ HN ₂ O ₄)]·7H ₂ O	1640br,s (COO ⁻), 1011(pyr)

a Varian Techtron AA-5, after digestion of the samples in concentrated HNO₃ of aqua regia.

Results and Discussion

Aqueous solutions of the complexes [Cu₂(PAP)(OH)X₃] (X = Cl, Br, IO₃) are sensitive to the presence of base and addition of *e.g.* aqueous ammonia, destroys the binuclear species producing [Cu(PAP – H)₂], which contains deprotonated ligand [9]. The sensitivity of the ligand itself to deprotonation can be best illustrated by examining the products of the reaction of PAP with a series of copper carboxylates in organic solvents. Complexes of the form [Cu₂(PAP – H)(RCOO)₃] result with acids whose pK_a is >3.8, while the complexes [Cu₂PAP(RCOO)₄] result with acids whose pK_a is <3.8 [9]. Also in mildly acidic solutions (pH < 3) the formation of mononuclear complexes involving protonated ligand groups was observed [10–13]. In order to minimise the possibility of decomplexation, with added anions which were likely to generate basic solutions, a near neutral buffer medium (phosphate, pH = 6.86) was used in some reactions. However, in certain cases this did not prevent ligand deprotonation and in others the same product resulted both in buffer and in water alone.

Compound **I** contains two nitrite groups and a hydroxy bridge (νOH, 3640 cm⁻¹) and the charge transfer band at 24100 cm⁻¹ (Table III) indicates the presence of deprotonated ligand [9]. Three prominent nitrite bands are observed in the infrared (Table II) and these are associated with terminal oxygen bonded nitrito groups [14]. The pyridine ring breathing absorption at 1014 cm⁻¹ indicates tetradentate coordination of the ligand [9]. The presence of a similar band in the spectra of the other PAP derivatives (with the exception of the perchlorate complexes where perchlorate vibrations mask this band) indicates that in these systems the ligand is tetradentate also. The presence of a shoulder at 17900 cm⁻¹ in the electronic spectrum of **I** is not structurally very informative, but may indicate the presence of distorted square planar copper(II) centres. The low room temperature magnetic moment indicates significant antiferromagnetic exchange between the two copper(II) centres, mediated by the hydroxide bridge. A structural representation for **I** is shown in Fig. 2.

Compound **II** appears to have a similar structure involving neutral ligand and a hydroxide bridge between the copper(II) centres. CN stretching absorptions associated with the thiocyanate groups indicate the presence of ionic and terminal N-bonded thiocyanate groups. This is in contrast to the nickel

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

Compound	d-d (cm ⁻¹)	CT (cm ⁻¹)	μ(BM) RT
I [Cu ₂ (PAP - H)(OH)(NO ₂) ₂] · 4H ₂ O	[17900]	24100	1.20
II [Cu ₂ (PAP)(OH)(NCS) ₃]	15200	28600	1.12
III [Cu ₂ (PAP - H)(N ₃) ₃] · H ₂ O	15900	25000	1.35
IV [Cu ₂ (PAP)(OH)Cl ₂] ClO ₄ · 5H ₂ O	14500, 16400	28600	1.13
V [Cu ₂ (PAP - H)Cl ₂ (H ₂ O)] ClO ₄	16300	25000[28600]	1.48
VI [Cu ₂ (PAP)(C ₂ O ₄) ₂]	15500	27800	1.97
VII [Cu ₂ (PAP - H)(OH)(HPO ₄)] · 1.5H ₂ O	[17500]	22700	1.69
VIII [Cu ₂ (PAP - H)(OH)(CNO) ₂]	15900	25000	1.20
IX [Cu ₂ (PAP - H)(SO ₄) _{1.5} · (H ₂ O)]	[13000], 15600	22700	1.91
X [Cu ₂ (PAP)(OH)(SO ₄) _{1.5} · (H ₂ O)]	14900	29000	1.26
XI [Cu ₂ (PAP - H)(OH) ₂ (H ₂ O)(ClO ₄)] · 5H ₂ O	[14900], [17900]	[23800]	1.24
XII [Cu ₂ (PAP)(OH)(CH ₃ COO)Cl ₂]	16000	27800	1.59
XIII [Cu ₂ (PAP)(OH)(C ₅ HN ₂ O ₄)(H ₂ O) ₂] · 7H ₂ O	[11000], 14500	27800	2.18
XIV [Cu ₂ (PAP)(OH)(C ₅ HN ₂ O ₄)] · 7H ₂ O	15900	27400	1.89

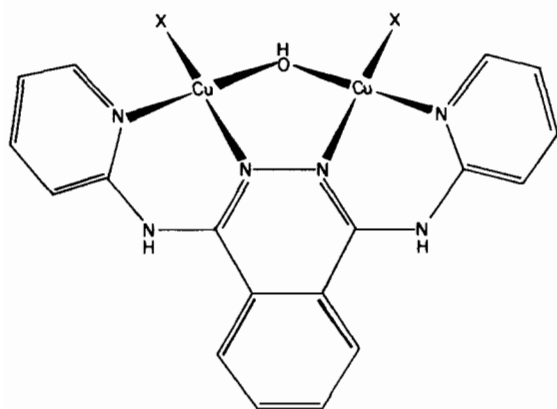


Fig. 2. Structural representation of the complex or complex ion in **I** ($X = \text{NO}_2^-$), **II** ($X = \text{NCS}^-$), **IV** ($X = \text{Cl}^-$), **V** ($X = \text{Cl}^-$, H_2O and $\text{OH}^- = \text{Cl}^-$), **VIII** ($X = \text{NCO}^-$).

complex $[\text{PAP}_2\text{Ni}_2(\text{NCS})_3]\text{NCS}$, which has a very low energy CN band (2002 cm^{-1}) associated with a $\mu\text{-N}$ thiocyanate group [12]. A distorted four coordinate structure is expected for this system and the low room temperature magnetic moment suggests significant spin exchange between the copper(II) centres.

The azide complex (**III**) has a weak infrared absorption at 3550 cm^{-1} , which could suggest the presence of a hydroxide bridge. However the low energy $\pi\text{-}\pi^*$ charge transfer band indicates that the ligand is present in its anionic form, if previous criteria are valid in this case, suggesting the absence of a hydroxide bridge [9]. Three prominent infrared bands in the range $2000\text{--}2083\text{ cm}^{-1}$, due to azide asymmetric N-N stretch, indicate the presence of more than one type of azide group. The complex

$[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Pd}_2(\text{N}_3)_6]$ has an azide bridged structure in which a terminal nitrogen atom on each bridge group acts as the bridging entity. The other azides act as terminal ligands in the dimeric structure [15]. Infrared bands, $\nu_{\text{as}}(\text{N}_3)$, for this system are found at 2060 , 2033 and 2000 cm^{-1} and the higher energy bands are associated with the bridge groups [16]. The most likely way in which an azide group could bridge the two copper centres in an intramolecular fashion in **III** would be as a single atom bridge. In recent papers dealing with end on (1,1) azide bridged systems triplet state stabilization was observed [17, 18], whereas with symmetrical end-to-end (1,3) bridging strong singlet state stabilization was observed [19, 20]. Also a view was expressed that an end on azido-bridge would most likely lead to a ferromagnetic interaction regardless of the Cu-N-Cu angle [18]. The low magnetic moment for **III** suggests fairly strong antiferromagnetic exchange with a singlet ground state.

Two basic structural possibilities are presented for **III**. The low magnetic moment could be due to the presence of a hydroxide bridge, in which case the low energy charge transfer band could be anomalous, and the structure could involve terminal azides at each copper(II) centre with the third azide acting as an ionic species or an additional end-on bridge. Alternatively a structure involving binuclear centres bridged in an intermolecular fashion by end-to-end azide groups and with no intramolecular hydroxide bridge could best interpret the physical data for this system. It is evident that with the paucity of infrared data on azide bridged species a clear cut distinction between the structural possibilities, in this case, is not possible using infrared measurements.

The perchlorate complexes **IV** and **V** were prep-

ared under different reaction conditions (pH 6.86 buffer for **V** and water for **IV**). A final solution pH of 3.0 resulted in the preparation of **IV** while the pH in the preparation of **V** was 6.0. Infrared data indicate the presence of a hydroxide bridge in **IV**, but no such bridge in **V**, and this is supported by the electronic spectral data, which indicate neutral ligand in **IV** and anionic ligand in **V** (the higher pH in this case is considered to be responsible for the ligand deprotonation). Ionic perchlorate groups appear to exist in both systems although the very broad ν_3 absorptions could possibly involve lower symmetry components indicative of weakly coordinated perchlorate groups. Infrared data support the presence of terminal copper–chlorine bonds in **IV** and both terminal and bridging copper–chlorine bonds in **V**. Significantly reduced magnetic moments are observed in both systems, but the very low moment for **IV** supports the presence of a hydroxide bridge. The reduced moment for **V** can be rationalized in terms of a chlorine bridge. Structurally compounds **IV** and **V** can be described in terms of a simple binuclear four-coordinate system (Fig. 2) in which $X = \text{Cl}$ for **IV** and $X = \text{Cl}$ and H_2O with a chloride bridge for **V**. In both cases the possible weak involvement of perchlorate as a bridging entity between the two copper centres should not be ignored.

The very insoluble oxalate complex, **VI**, has no hydroxide bridge, but has neutral ligand and a magnetic moment indicative of the absence of antiferromagnetic exchange. A polymeric structure is suggested for this system, in which the binuclear integrity of the Cu_2PAP unit is maintained but with intermolecular oxalate bridges. A very strong, broad antisymmetric $\text{C}=\text{O}$ stretching absorption is observed in the infrared, centred at about 1670 cm^{-1} , but this and other oxalate absorptions are not very informative in terms of the actual bonding role of the oxalate groups.

Reaction of $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ with HPO_4^{2-} in phosphate buffer (pH 6.86) leads to an insoluble complex which, according to microanalysis and other data, has a hydroxide bridge and an anionic ligand and includes the ion HPO_4^{2-} . The slightly reduced magnetic moment suggests weak antiferromagnetic exchange and the very rich infrared absorption in the range $1075\text{--}965\text{ cm}^{-1}$ suggests the presence of a low symmetry phosphate group, possibly a bridging entity between the two copper(II) centres. The presence of other polyatomic anion bridges *e.g.* SO_4^{2-} , NO_3^- , IO_3^- in other similar complexes [6, 8] indicates that a hydrogen-phosphate group could act as an intramolecular bidentate (O,O) bridge. The orthogonality of the phosphorus sp^3 hybrid orbitals in such a phosphate group could lead to a situation in which, as a bridging entity, a ferromagnetic interaction between *e.g.* two copper(II) centres could result. This combined with

an antiferromagnetic spin exchange *via* the hydroxide bridge could lead to a situation where the net reduction in magnetic moment is reduced at room temperature. In the phosphate bridged copper(II) dimer, $[\text{Cu}(5'\text{-UMP})(\text{dpa})(\text{H}_2\text{O})]_2 \cdot 5\text{H}_2\text{O}$ ($5'\text{-UMP}$ = uridine- $5'$ -monophosphate and dpa = 2,2'-dipyridylamine), in which the copper-copper separation is 5.12 \AA , a weak antiferromagnetic exchange exists ($-J = 5.4\text{ cm}^{-1}$) with a room temperature magnetic moment of $>1.75\text{ BM}$ [21]. A reasonable structural representation for **VII** would be a five-coordinate system with an intramolecular hydrogen phosphate bridge, a coordinated water molecule at one copper centre and an oxygen atom from a phosphate group in a neighbouring molecule coordinated to the fifth site at the other copper centre. A similar structure was found for the complex $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ [8] involving both intramolecular and intermolecular sulphate bridging. It is of interest to note that addition of HPO_4^{2-} is not necessary to produce this complex; **VII** crystallizes out of the buffer itself after dissolving $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$.

The cyanate complex, **VIII**, which was prepared in buffer, has both a hydroxide bridge and an anionic ligand, despite the near neutral reaction conditions (pH 6.45). A very sharp band at 3580 cm^{-1} leaves no doubt as to the presence of the hydroxide bridge and two νCN bands, associated with the cyanate groups, suggest the presence of N-bonded terminal cyanate groups. The very low room temperature magnetic moment, again indicative of antiferromagnetic exchange, supports the presence of the hydroxide bridge. Structurally compound **VIII** can best be represented as a binuclear four-coordinate system (Fig. 2; $X = \text{CNO}^-$).

It has been shown that by using the neutral ligand complex $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ as a starting material both neutral and anionic ligand complexes can be produced, depending on the prevailing pH conditions and the ion in question. The complex $[\text{Cu}_2(\text{PAP} - \text{H})(\text{CH}_3\text{COO})_3]$, which has an anionic ligand, was used in two cases involving the sulphate and perchlorate anions. Compound **IX** has an anionic ligand and does not have a hydroxide bridge and the rather complex ν_3 sulphate absorptions in the infrared suggest the presence of low symmetry, coordinated sulphate groups. In a related complex, $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ [8], the sulphate group has a dual role, as an intramolecular bridge between the copper(II) centres, and, using a third oxygen atom, as an intermolecular bridge. In this system four major ν_3 sulphate bands are observed in the infrared at 1140 , 1116 , 1030 and 960 cm^{-1} . The 'normal' magnetic moment associated with **IX** supports the absence of a hydroxide bridge.

In contrast to **IX** compound **X**, which was prepared by direct reaction of copper sulphate and PAP in water, has a neutral ligand, a hydroxide bridge

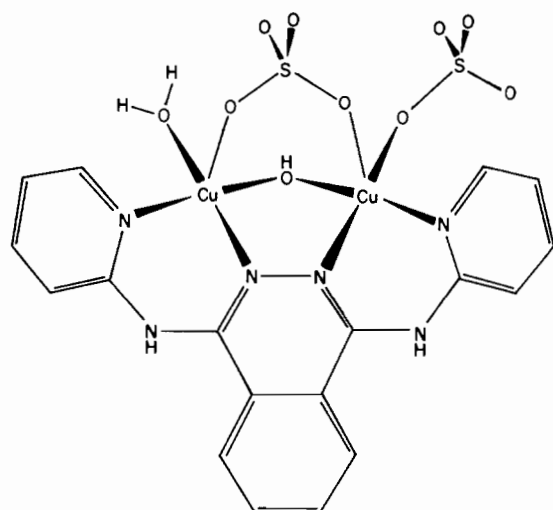


Fig. 3. Structural representation for **X**.

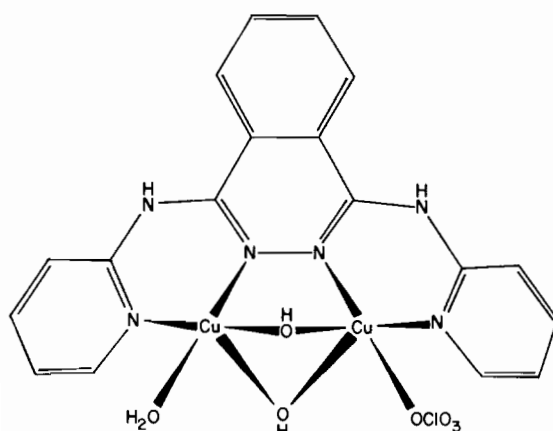


Fig. 4. Structural representation for **XI**.

and a very low magnetic moment indicative of a fairly strongly antiferromagnetically coupled system. Again a rather complex infrared absorption, associated with the sulphate groups, indicates low symmetry, coordinated anions. By analogy with the complex $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}(\text{SO}_4)] \cdot 2\text{H}_2\text{O}$ [8] **X** must involve an intramolecular sulphate bridge between the two copper centres in order to create a large enough oxygen bridge angle to produce such a low magnetic moment [8]. The other sulphate probably bridges two binuclear units, while the fifth coordination site at one copper centre is occupied by a water molecule (Fig. 3). Complex **IX** may have a similar structural arrangement but without a hydroxide bridge and involving four-coordinate copper centres.

The perchlorate complex **XI** is unusual in that it appears to be a di- μ -hydroxo bridged system and also has an anionic ligand. The low magnetic moment would certainly be typical of such a system. Two major infrared absorptions are observed, associated

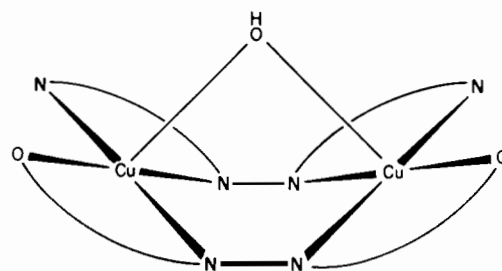


Fig. 5. Structural representation for the binuclear centre in **XIII**. ONNO represents pyrazole dicarboxylic acid trianion.

with the perchlorate group at 1130 and 1070 cm^{-1} , suggesting a coordinated anion. Fig. 4 illustrates a proposed structural representation for **XI** involving five-coordinate copper(II) centres, a monodentate perchlorate and a coordinated water molecule. This complex represents somewhat of a departure from the norm with systems of this sort, because only monohydroxo-bridged complexes have been reported so far.

Compound **XII** was prepared by dissolving $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ in aqueous ammonium acetate (pH 7.0) resulting in partial displacement of chlorine by acetate. The complex has a hydroxide bridge and neutral ligand and infrared bands at 1573 and 1400 cm^{-1} are assigned to antisymmetric and symmetric stretch respectively in a bridging carboxylate [9]. Two far infrared bands at 308 , 290 cm^{-1} are assigned to terminal copper-chlorine bonds. Structurally this compound appears to be analogous to the parent derivative $[\text{Cu}_2(\text{PAP})(\text{OH})\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$ but with the bridging chlorine replaced by a carboxylate [22] (Fig. 4, but with H_2O and ClO_4^- replaced by Cl^- and a bidentate carboxylate replacing the axially bound hydroxide).

The two complexes involving pyrazole-3,5-dicarboxylic acid are both hydroxide bridged derivatives, although no infrared absorption associated with this group can be discerned in the broad strong envelope in the range $3300\text{--}3500\text{ cm}^{-1}$ observed in both cases. Since neutral ligand is present in both systems and chlorine is absent (elemental analysis) the pyrazole ligand is bound as a trianion (PDC^{3-}). The only reasonable way to accommodate both PAP and PDC^{3-} at the same binuclear centre would be in a hydroxide bridged boat structure (Fig. 5) involving square pyramidal copper centres and the involvement of PDC^{3-} as a tetradentate ligand. Molecular models indicate this to be an unstrained arrangement if the oxygen bridge angle is around 90 degrees. Complexes **XIII** and **XIV** clearly differ in terms of the involvement of a water molecule as a sixth ligand at each copper centre in **XIII**, which are absent in **XIV**. The water is readily removed by heating under vacuum, although other water molecules are more tightly bound. The 'normal' magnetic moments

observed for both complexes can be attributed to a small angle at the bridging hydroxide in keeping with the structural predictions.

This study has shown that a variety of anionic groups can be incorporated into the basic binuclear unit $[\text{Cu}_2(\text{PAP})(\text{OH})]^{n+}$ as terminal and bridging entities. Low magnetic moments are observed for most complexes containing hydroxide bridges and in four cases (I, II, IV, VIII) moments of 1.2 BM or less are observed. These complexes appear to have double bridged structures involving the phthalazine diazine bridge and a hydroxide bridge and have room temperature moments which are smaller than those observed for analogous triple bridged derivatives, in which the third bridge is a single atom entity (e.g. Cl, Br) [7, 8]. Linear relationships have been observed between $-2J$ and oxygen bridge angle and room temperature magnetic moment and oxygen bridge angle for anion bridged complexes $[\text{Cu}_2(\text{PAP})(\text{OH})\text{X}]^{n+}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-, \text{SO}_4^{2-}$), which have $d_{x^2-y^2}$ ground states, [7] and if one projects data for compounds I, II, IV, VIII onto the magnetic moment plot bridge angles for these systems could be in excess of 110 deg. This would suggest that an expanded binuclear centre exists in the double bridged systems, with dimensions comparable to those in cases where large bridge groups e.g. NO_3^- , SO_4^{2-} , exist in the triply bridged structures. The complex $[\text{Cu}_2(\text{MIP})(\text{OH})\text{Cl}_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ [7] (MIP = 1,4-di(1'-methyl-2'-imidazolyl)phthalazine) has a diazine bridge and a hydroxide bridge and five-membered chelate rings, rather than the six-membered rings present in the PAP complexes. Here a very low moment ($\mu_{\text{RT}} = 0.62$ B.M.) and large antiferromagnetic exchange ($-2J = 800 \text{ cm}^{-1}$) are observed for a system with a large bridge angle (Cu—O—Cu 126.2 deg). The presence of five-membered chelate rings would, of necessity, lead to an expanded binuclear centre in comparison with I, II, IV and VIII. Extrapolation of the μ vs. Cu—O—Cu plot [7] to include the pyrazole dicarboxylate complexes (XIII, XIV) shows that for room temperature magnetic moments of 1.9–2.0 B.M. oxygen bridge angles of around 90 deg would be expected.

Even in the absence of structural data it is clear that by varying the anionic ligands in the basic unit $[\text{Cu}_2(\text{PAP})(\text{OH})]^{n+}$ significant changes in the dimensions of the binuclear centre can be effected as reflected by the values of the room temperature magnetic moments. We await structural and variable temperature magnetic studies on a number of these systems to further substantiate the linear relation-

ship already observed between exchange and oxygen bridge angle for systems of this sort.

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