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Metal chelates of *N*-(2-pyridylmethyl)iminodiacetate(2-) ion (pmda). Part I. Two mixed-ligand copper(II) complexes of pmda with *N*,*N*-chelating bases. Synthesis, crystal structure and properties of $H_2pmda\cdot 0.5H_2O$, $[Cu(pmda)(pca)]\cdot 3H_2O$ (pca = α-picolylamine) and $[Cu(pmda)(Hpb)]\cdot 5H_2O$ (Hpb = 2-(2′-pyridyl)benzimidazole)

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Abstract

N-(2-Pyridylmethyl)iminodiacetic acid hemi-hydrate ($H_2pmda\cdot 0.5H_2O$) was prepared and characterized by X-ray crystallography (final $R1 = 0.042$). The zwitterion $H_2pmda^{\pm}$ is *intra*-stabilized by a trifurcated hydrogen bond. Intermolecular carboxylic-carboxylate hydrogen bonds and the parallel inter-ligand π,π-stacking (3.57(2) Å) between pyridyl rings from pairs of adjacent zwitterions generate 2D frameworks (bi-layers with the carboxyl groups towards the external surfaces and py–pmda rings towards the inside). In the crystal, the bi-layered structures are connected by equivalent hydrogen bonds, which link each water molecule to two symmetry related O-carboxylate atoms from the adjacent external faces of two 2D frameworks. The compounds $[Cu(pmda)(pca)]\cdot 3H_2O$ (**1**) and $[Cu(pmda)(Hpb)]\cdot 5H_2O$ (**2**) were obtained by stoichiometric reaction of $Cu_2(CO_3)(OH)_2$, $H_2pmda\cdot 0.5H_2O$ and α-picolylamine (pca) or 2-(2′-pyridyl)benzimidazole (Hpb), respectively, and characterized by single crystal X-ray diffractometry. Compound **2** was also studied by TG analysis (with FTIR study of the evolved gasses in the pyrolysis), magnetic susceptibility at 80–300 K range, and FTIR, electronic, ESR spectra. In **1** and **2** the copper(II) atom exhibits a distorted octahedral coordination (type 4+1+1) and pmda acts as tripodal tetra-dentate ligand. However, pmda displays different coordination roles. The pmda supplies two *N*,*O*-meridional and two *trans*-apical *N*(py),*O*-donors in **1**, whereas links the metal by three *N*,*N*(py),*O*-meridional and one *O*-apical atoms in **2**. No π,π-stacking of pyridyl–(pmda) rings is observed in these complexes. The pyridyl–(pca) ring of **1** is not involved in ring–ring stacking interactions, but compound **2** recognizes itself by a roughly anti-parallel π,π-stacking of adjacent Hpb ligands (5.3°, 3.41(2) Å) forming pairs of complex units.

Keywords: Copper(II); *N*-(2-Pyridylmethyl)iminodiacetic acid; *N*-(2-Pyridylmethyl)iminodiacetate(2-) ion; 2-(Aminomethyl)pyridine; α-Picolylamine; 2-(2′-Pyridyl)benzimidazole; Crystal structures; Mixed-ligand complexes; Aromatic π,π-staking interactions; Molecular recognition; Thermal stability; Spectral and magnetic properties

1. Introduction

The structure of poly-{diaqua(iminodiacetato)copper(II)}, $\{[Cu(IDA)(H_2O)_2]\}_n$, was reported by different groups [1]. This compound is a ‘reference’ complex for a variety of ternary mixed-ligand Cu(II) complexes having iminodiacetate (IDA) and N-heterocyclic donors or closely related ligands. The structures of these com-

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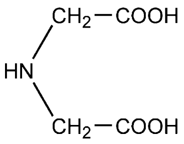
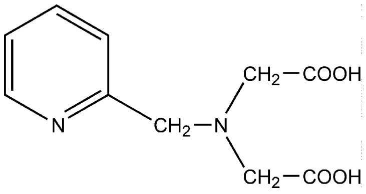
pounds have afforded various structural co-relations. For example, IDA (or IDA-like) conformation changes from *fac*- to *mer*-conformation when aqua is replaced in [Cu(IDA)$(H_2O)_2$] (or a related chelate) by a monodentate N-heterocyclic imidazole (Him) or Him-derivative. Subsequently, a *mer*- to *fac*-IDA (or IDA-like) conformation is systematically observed going from these 1/1/1 Cu–IDA–N-heterocyclic donor compounds [1c,2–11] to others having a 1/1/2 Cu–IDA–N-heterocyclic donor ratio [12,13] or closely related complexes [14–17]. Some of these later compounds [14,15,17] reveal in addition that in the secondary ligand there is a preference of the N-heterocyclic donor for the *trans*-position to the Cu–N(IDA or IDA-like) bond. In this broad context, we became increasingly interested on new mixed-ligand copper(II) complexes having a *N*-R-IDA derivative with a R non-chelatable [16,17] or chelatable [18]18a aromatic side chain as primary ligand, and various N-heterocyclic secondary ligand of remarkable aromaticity. These kinds of mixed-ligand complexes could be 'structural model systems' with possibilities of displaying 'aromatic π,π-stacking interaction's. Such weak interactions are extensively studied because they seem to play essential roles in molecular recognition processes and in supra-molecular assemblies of relevant biological (and non-biological) systems [19,20].

It is well known that 2-(aminomethyl)pyridine or α-picolyamine (pca) acts as *N,N*-bidentate diamine ligand for copper(II) in $[Cu(pca)_3]Cl_2 \cdot Cl_2CH_2$ [21a] and in several 'mixed-ligand' complexes (such as, $[Cu(pca)_2(H_2O)_2]Cl_2$ [21b] or $[Cu(pca)_2(L)_2]$ (L = various anions) both in solution and/or in solid state [21c,21d,21e,21f,21g,21h,21i]. Pyridyl π,π-stacking interactions have recently been reported for a polymeric non-chelated pca–silver(I) complex [22]. In this sense, a suggestive H_2IDA-derivative (as primary ligand) is the anion of *N*,*N*-bis(carboxymethyl)-2-(aminomethyl)pyridine or *N*-(2-pyridylmethyl)iminodiacetic acid (H_2pmda), namely *N*-(2-pyridylmethyl)iminodiacetate(2-) (hereafter pmda) (Schemes 1 and 2).

The stability constants of pmda-complexes in solution have been reported for a large variety of mono-(Li, Na, Ag, Tl), di-(alkaline-earths, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pb), tri-(lanthanide series, Am, Cm) and tetravalent (vanadyl) metal ions [23]. As expected, the tripodal pmda ligand forms a very stable Cu(II) chelate ($\log K = 14.2$ at 20 °C) [23d,23h,23i]. Crystal structure reports on pmda-derivatives are surprisingly limited to one dinuclear complex of iron(III) [24], two vanadium compounds [25] and a tricarbonyl–technetium derivative [26]. In these cases pmda acts as tetradentate, but no mention is made of 'aromatic ring stacking' interactions. In contrast, we have recently found that in the polymeric structure of $\{[Cu(pmda)] \cdot 2H_2O\}_n$ there is a multi-π,π-stacking interaction between pyridyl rings of the complex chains [18b]. This paper deals with the synthesis and molecular and crystal structure of the free acid ($H_2pmda \cdot 0.5H_2O$) and of two pmda–copper(II) chelates having pca or 2-(2′-pyridyl)benzimidazole (Hpb) as secondary ligand. The aim of the present work is to study the coordination preferences of N donor atoms of these unsymmetrical diamines to the *trans*-position versus the Cu–N(tertiary amino pmda) bond. The inter-ligand aromatic ring π,π-stacking interactions in the studied compounds are also discussed (Schemes 3 and 4).



Scheme 1. H_2IDA.

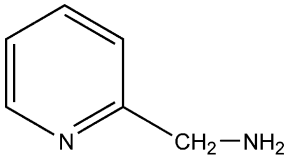


Scheme 2. H_2pmda.

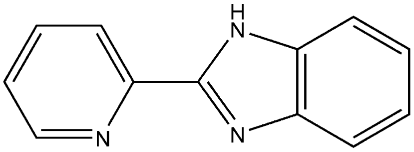
2. Experimental

2.1. Synthesis of the acid $H_2pmda \cdot 0.5H_2O$

The pmda ligand has been obtained as free acid by reaction of potassium chloroacetate and pca in aqueous alkaline solution at room temperature (r.t.). In a standard essay the solution of chloroacetic acid (79.36 g, 0.84 mol) in 200 ml of water was stirred and cooled in a salt–ice bath. A solution of KOH (94.08 g, 1.68 mol) in 200 ml of water was drop-wise added. To the resulting alkaline solution pca (41.24 ml, 0.40 mmol) was slowly added and the mixture was left to react in a 500 ml cooled flask in the dark for 2 weeks. HCl 6N (33 ml) was added to neutralize the solution, which was concentrated under reduced pressure and cooled (salt–ice bath) to remove KCl (by-product, 40 g). HCl 6N was newly added to fit the pH near 2.5. The desired acid precipitates and is removed by filtration. An additional amount of HCl 6N was added to the mother liquor (pH ~4) to bring down the pH to 2.5. A new amount of



Scheme 3. Pca.



Scheme 4. Hpb.

H_2pmda was removed by filtration. The product was re-crystallized in a hot fifty–fifty ethanol–water mixture, filtered and air-dried. Many well-shaped prismatic crystals of $H_2pmda \cdot 0.5H_2O$ suitable for crystallographic work were obtained in this way. This product can also be re-crystallized from water or water:methanol (1:4). Yield: 50.38 g, 54%. *Anal.* Calc. for $C_{10}H_{12}N_2O_4 \cdot 0.5H_2O$: C, 51.50; H, 5.62; N, 12.01. Found: C, 51.41; H, 5.68; N, 11.96%. Alternative syntheses of this acid were reported in the literature [23i,27]. ^{1}H NMR (300 MHz, *d*6-DMSO; δ, ppm): 3.47 (s, 4H), 3.97 (s, 2H), 7.27 (m, 1H), 7.53 (d, 1H), 7.77 (m, 1H), 8.46 (d, 1H) and 11.99 (exchangeable H). ^{13}C NMR (d_6-DMSO; δ, ppm): 54.44 ($N-CH_2-COO^-$), 59.01 ($C_{arom}-CH_2-N$), 122.29, 122.71, 136.64, 148.44 and 158.98 (C_{arom}), and 172.47 ($-COO^-$). FTIR spectrum (cm^{-1}): 3449, ν(OH); 3110, $\nu(CH_{arom})$; 3065 and 3002 $\nu_{as}(CH_2)$; 2964, $\nu_s(CH_2)$; 1690 and shoulders, ν(C=O), pyridyl ring breathing I and $\delta(H_2O)$; 1595, ν_{as}(COO) and pyridyl ring breathing II; 1480, pyridyl ring breathing III; 1437, pyridyl ring breathing IV, and 1389, ν_s(COO). TG+FTIR of pyrolysis gasses: In a dry-air flow it becomes nearly anhydrous (water: 0.58% exp., calc. 3.86%) and the anhydrous sample gives three pyrolytic steps (190–575 °C) with production of H_2O, CO_2, CO, NH_3 and N_2O. The decomposition starts by de-carboxylation of a free carboxylic group (190–200 °C).

2.2. Synthesis of [Cu(pmda)(pca)]·3H₂O

The stoichiometric reaction of bluish copper(II) hydroxycarbonate ($Cu_2(CO_3)(OH)_2$) and ($H_2pmda \cdot 0.5H_2O$) in water yields a blue solution of the complex [Cu(pmda)(H_2O)$_2$] (from which a polymeric solid $\{[Cu(pmda)] \cdot 2H_2O\}_n$ could be obtained [18b]). In a typical essay a mixture of 466.4 mg (2.0 mmol) of $H_2pmda \cdot 0.5H_2O$ and 221.1 mg (1.0 mmol, Probus) of $Cu_2CO_3(OH)_2$ in 150 ml of water was heated and stirred under controlled vacuum (to remove the CO_2, by-product). The solution was stirred and heated at 60 °C for 30 min, left to cool at r.t. and then slowly filtered to remove any insoluble by-product (mainly a small amount of CuO). The clear blue solution was stirred and 0.21 ml (2 mmol, Aldrich) of pca was drop-wise added. By slow evaporation of the solution at r.t. the volume was reduced to a few millilitres, and then isopropanol and acetone was added just to initiate the precipitation. The crystallization device was covered with a watch glass and slowly evaporated. A very variable and limited amount of needle-shaped crystals of the desired product (compound **1**) were formed, many of them being poly-crystals. Some single crystals were picked up for the X-ray diffraction study. The remaining product was filtered-off and air-dried for elemental analysis and FTIR spectral characterization. Frequently the reaction mixture is degraded, probably by pca oxidation, which is observed from a change from blue to greenish color. These changes are promoted by heating. Yield: < 5%. *Anal.* Calc. for $C_{32}H_{48}Cu_2N_8O_{14}$: C, 42.90; H, 5.40; N, 12.51. Found: C, 42.96; H, 5.44; N, 12.56%. The FTIR spectrum (cm^{-1}): ~3400 and 1629, ν and $\delta(H_2O)$; 3263, 3130 and 1571, ν_{as}, ν_s and $\delta(NH_2)$; 3083 and 3058, $\nu(CH_{arom})$; 2978, $\nu_{as}(CH_2)$; 2863, $\nu_s(CH_2)$; 1680, pyridyl ring breathing I; 1608, ν_{as}(COO) and pyridyl ring breathing II; 1482, pyridyl ring breathing III; 1446 or 1438, pyridyl ring breathing IV; and 1394, ν_s(COO). $\Delta(COO) = 214\ cm^{-1}$.

2.3. Synthesis of [Cu(pmda)(Hpb)]·5H₂O

To a clear blue solution of pmda–Cu(II) complex prepared in 200 ml of water, as referred before, 390.5 mg of Hbp (1 mmol, Aldrich) was added. The mixture was stirred 48 h at r.t. and filtered, and the blue solution was left to evaporate in a crystallization device. After 2 weeks, blue crystals of the desired product (compound **2**) were formed, some of them suitable for X-ray crystallography. The product was collected by filtration, washed with water and ethanol, and air-dried. Successive amounts of **2** can be collected. The product can be re-crystallized several times from water. Yield: 75%. *Anal.* Calc. for $C_{22}H_{29}CuN_5O_9$ C, 46.27; H, 5.12; N, 12.26; Cu, 11.13. Found: C, 46.46; H, 5.46; N, 12.48; Cu, 10.93% (EDTA complexometry [1,15]). FTIR spectrum data (cm^{-1}): ~3420 $\nu_{as}(H_2O)$; 3263(broad), $\nu_s(H_2O)$ and ν(NH) of Hpb; 3098 and 3060, $\nu(CH_{arom})$; 2977 and 2926, $\nu_{as}(CH_2)$; 2861 and 2813, $\nu_s(CH_2)$; 1639, pyridyl ring breathing I and $\delta(H_2O)$; 1613, ν_{as}(COO) and pyridyl ring breathing II; 1598, ν_{as}(COO); 1541, δ(NH) of Hpb; 1482, pyridyl ring breathing III; 1443 or 1425, pyridyl ring breathing IV; 1394 and 1382, ν_s(COO). $\Delta(COO) = 219–216\ cm^{-1}$.

2.4. X-ray data collection, solution of the structures and refinement

2.4.1. Acid H₂pmda·0.5H₂O

A colorless prismatic crystal of $H_2pmda \cdot 0.5H_2O$ was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range of $12.152° < \theta < 42.972°$ in an Enraf–Nonius CAD4 diffractometer [28]. Data were collected at 293 K using Cu

Kα radiation ($\lambda = 1\ 54\ 184$ Å) and the ω-scan technique and corrected for Lorentz and polarization effects [29]. A semi-empirical absorption correction (Psi-scans) was made [30]. The structure was solved by direct methods [31], which revealed the position of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-square procedure using anisotropic displacement parameters [32]. All hydrogen atoms were located from difference maps and refined isotropically. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [33]. Molecular graphics plotted from PLATON-98 [34]. A summary of the crystal data, experimental details and refinement results is given in Table 1.

2.4.2. *[Cu(pmda)(pca)]·3H$_2$O and [Cu(pmda)(Hpb)]·5H$_2$O (compounds **1** and **2**)*

Crystallographic data for these two blue compounds were collected on a Bruker Smart CCD diffractometer at 293 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), and were corrected for Lorentz and polarization effects. The frames were integrated with the Bruker SAINT [35a]; software package and the data were corrected for absorption using the program SADABS [35b]. The structures were solved by direct methods using the SHELXS-97 program [36]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL-97 [37]. The position of most H atoms was calculated geometrically and included in structure factor calculations, but in compound **2** the H atom bonded to N23 was located in difference maps and its position was refined isotropically. Crystal data and structure refinement parameters are listed in Table 1. Molecular graphics were obtained using SHELXTL [38].

2.5. *Physical measurements*

NMR spectra were recorded in a Bruker AM300 spectrophotometer. Infrared spectra were obtained by the KBr disc technique on a JASCO FTIR 410 instrument. In addition the TG (pyrolysis) of studied compounds and analysis of evolved gasses were recorded (295–775 K) in air flow (100 ml min^{-1}) using a Shimazu Thermobalance TGA-DTG-50H coupled with an IRFT Nicolet Magma 550 (and mass spectrometer Fisons Thermolab). Electronic (reflectance) spectra (175–3300 nm) were obtained in a Cary 5E spectrophotometer.

Table 1
Crystal data and structure refinement for compounds H_2pmda·H_2O, [Cu(pmda)(pca)(H_2O)]·3H_2O (**1**) and [Cu(pmda)(Hbp)]·5H_2O (**2**)

	H_2pmda·0.5H_2O	Compound **1**	Compound **2**
Empirical formula	$C_{10}H_{13}N_2O_{4.5}$	$C_{16}H_{24}CuN_4O_7$	$C_{22}H_{19}CuN_5O_9$
Formula weight	233.22	895.86	571.04
Temperature (K)	293(2)	293(2)	293(2)
Wave length (Å)	1.54184	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	28.655(4)	15.612(1)	11.632(1)
b (Å)	5.7937(3)	7.833(1)	9.285(1)
c (Å)	12.4235(3)	32.678(2)	23.344(2)
β (°)	114.42(1)	98.95(1)	92.19(1)
Volume (Å^3)	2151.8(5)	3947.6(4)	2519.4(3)
Z	8	8	4
D_{calc} (Mg m^{-3})	1.440	1.507	1.505
Absorption coefficient (mm^{-1})	0.975	1.152	0.927
$F(000)$	984	1864	1188
Crystal size (mm)	0.35 × 0.15 × 0.10	0.42 × 0.29 × 0.16	0.36 × 0.15 × 0.15
θ Range for data collection (°)	3.39–74.24	1.55–28.02	1.75–28.03
Index ranges	$0 < h < 35$, $0 < k < 7$, $-17 < l < 16$	$-9 < h < 20$, $-9 < k < 10$, $-42 < l < 42$	$-15 < h < 15$, $-11 < k < < 12$, $-30 < l < 24$
Reflections collected/unique	2238/2193, [R(int) = 0.0127]	22679/9028, [R(int) = 0.0404]	14863/5848, [R(int) = 0.0480]
Completeness (to 2θ)	45.2% (74.24)	94.4% (28.02)	95.8% (28.03)
Absorption correction	Psi-scan	empirical (SADABS)	empirical (SADABS)
Max/min transmission	0.965, 0.916	1.0000, 0.7485	1.0000, 0.7908
Refinement method	full-matrix least-square F^2	full-matrix least-square F^2	full-matrix least-square F^2
Data/restraints/param.	2193/0/200	9028/0/505	5848/0/338
Goodness-of-fit on F^2	1.038	0.913	0.960
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.042$, $wR_2 = 0.112$	$R_1 = 0.042$, $wR_2 = 0.099$	$R_1 = 0.053$, $wR_2 = 0.137$
R indices (all data)	$R_1 = 0.055$, $wR_2 = 0.121$	$R_1 = 0.084$, $wR_2 = 0.108$	$R_1 = 0.102$, $wR_2 = 0.152$
Extinction coefficient	0.0046(3)	none	none
Largest difference on peak and hole (e Å^{-3})	0.703/−0.304	0.534/−0.436	0.616/−0.243

RSE spectra of a polycrystalline sample were recorded without magnetic dilution in a spectrophotometer Bruker ESP 300E (X band) at r.t. The magnetic susceptibility of **I** was measured at the temperature range 80–300 K using a Manics DM magnetometer. The susceptometer was calibrated with mercury tetrakis(thiocyanato)–cobaltato(II). Corrections for the diamagnetism ($122\cdot10^{-6}$ cm^3 mol^{-1}) were estimated from Pascal constants [39]. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1} per Cu(II) atom) [40].

3. Results and discussion

3.1. Description of the structures

Bond lengths and angles between non-hydrogen atoms and hydrogen bond distances and angles of $H_2pmda\cdot0.5H_2O$ are given in Table 2. Fig. 1 shows a drawing of two adjacent symmetrically related units, with the numbering scheme. According to the relative magnitude of its pK_a values (for example, p$K_0 = 2.65$, p$K_1 = 2.74$ and p$K_2 = 8.16$ for a proton dissociation from H_3pmda^+, H_2pmda and $Hpmda^-$, respectively, at $I = 0.1$(KNO_3) and 25 °C [23d]) the molecule of this diamino-diacid will exist as a zwitterion in solution of polar solvents. Such dipolar ions $H_2pmda^{\pm}$ are also found in the crystal, as it has usually been observed for a variety of free amino-polycarboxylic acids [41].

Two structural features of the studied amino-polycarboxylic acid are of major interest. First, is the conformation intra-stabilised by a trifurcated hydrogen bond formed by the 'onium' proton with two carboxylate atoms, O(12) and O(22), and the pyridyl atom N(2) as 'acceptors'. In accordance, its planar pyridyl ring forms similar dihedral angles with the planes of both carboxylic (86.2°) and carboxylate (89.3°) groups. Similar kind of zwitterions have been largely referred for the structure of a variety of amino-polycarboxylic acids such as iminodiacetic acid [41]. The presence of similar trifurcated hydrogen bonds governing a zwitterion conformation is also known, for example, in the crystal structures of β-(hydroxyethyl)iminodiacetic acid (H_2heida) [42] and nitrilopropionicdiacetic acid (H_3npda) [43], both with appropriate O-acceptor atoms in the 'third arm'. In H_2heida the 'onium' hydrogen atom interacts with two O-carboxyl and one O-alcoholic atoms, whereas in H_3npda three O-carboxyl atoms interact with the onium $N{-}H^+$ group. Second, pyridyl rings from pairs of adjacent dipolar ions $H_2pmda^{\pm}$ (related by the symmetry code $\#2 = ii = 1/2-x,\ -1/2-y,\ 2-z$) lie parallel and stacked (dihedral angle between planes $\alpha = 0.2°$) at a distance of 3.57(1) Å (Fig. 1). This

Table 2
Bond lengths (Å) and angles (°) and data concerning hydrogen bonds in $H_2pmda\cdot0.5H_2O$ with e.s.d. in parentheses

Bond lengths				
O(11)–C(12)	1.299(2)	N(2)–C(6)	1.341(2)	
O(12)–C(12)	1.207(2)	C(1)–C(2)	1.506(2)	
O(21)–C(22)	1.234(2)	C(2)–C(3)	1.387(3)	
O(22)–C(22)	1.268(2)	C(3)–C(4)	1.381(3)	
N(1)–C(11)	1.492(2)	C(4)–C(5)	1.378(3)	
N(1)–C(1)	1.495(2)	C(5)–C(6)	1.379(3)	
N(1)–C(21)	1.497(2)	C(11)–C(12)	1.512(2)	
N(2)–C(2)	1.337(2)	C(21)–C(22)	1.520(2)	
Bond angles				
/c>				
C(11)–N(1)–C(1)	112.4(2)	C(4)–C(5)–C(6)	118.4(2)	
C(11)–N(1)–C(21)	111.5(2)	N(2)–C(6)–C(5)	123.6(2)	
C(1)–N(1)–C(21)	111.1(2)	N(1)–C(11)–C(12)	109.2(2)	
C(2)–N(2)–C(6)	117.2(2)	O(12)–C(12)–O(11)	126.7(2)	
N(1)–C(1)–C(2)	111.6(2)	O(12)–C(12)–C(11)	121.9(2)	
N(2)–C(2)–C(3)	123.1(2)	O(11)–C(12)–C(11)	111.5(2)	
N(2)–C(2)–C(1)	117.3(2)	N(1)–C(21)–C(22)	111.8(2)	
C(3)–C(2)–C(1)	119.6(2)	O(21)–C(22)–O(22)	127.2(2)	
C(4)–C(3)–C(2)	118.5(2)	O(21)–C(22)–C(21)	117.2(2)	
C(5)–C(4)–C(3)	119.2(2)	O(22)–C(22)–C(21)	115.6(2)	
Hydrogen bonds				
D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(1)···N(2)	0.94(2)	2.32(2)	2.687(2)	102.3(2)
N(1)–H(1)···O(12)	0.94(2)	2.23(2)	2.669(2)	107.4(2)
N(1)–H(1)···O(22)	0.94(2)	2.28(2)	2.680(2)	105.0(2)
O(11)–H(11)···O(22)#1 [a]	1.12(4)	1.38(4)	2.479(2)	165.0(3)
O(1)–H(1O)···O(21)#1 [a]	1.12(2)	1.77(2)	2.830(2)	157.4(1)

[a] Symmetry code: $\#1 = x,\ -y+1,\ z-1/2$.

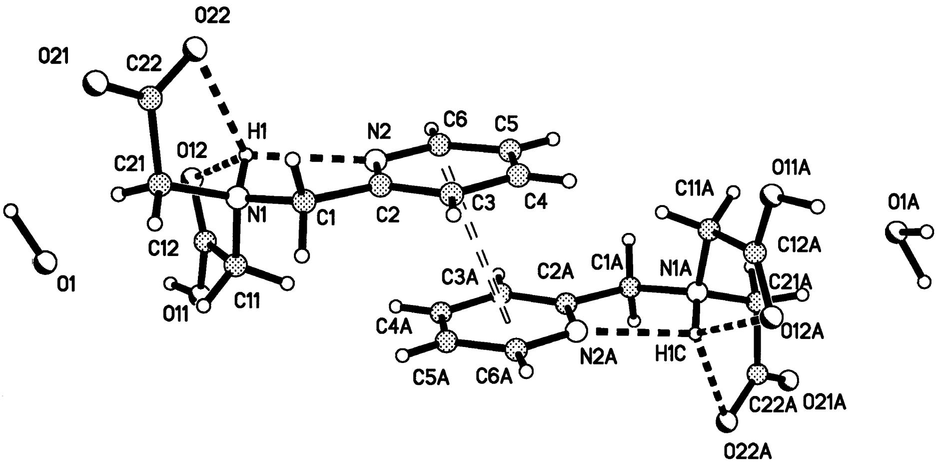
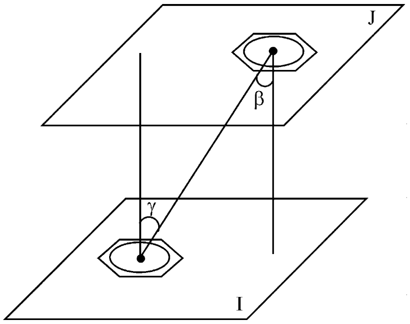


Fig. 1. Structure of the acid *N*-(2-pyridylmethyl)iminodiacetic acid hemi-hydrate showing the stacking between pyridyl rings of two adjacent zwitterions, which are intra-stabilised by a tri-furcated hydrogen bond.



Scheme 5. β and α angles in a ring–ring π,π-stacking interaction.

π,π-interaction will have a significant σ,π-contribution because of the long centroid–centroid distance (3.94 Å) and the remarkable displacement between the stacked rings (angles of the centroid–centroid vector with the perpendicular to each stacked ring plane are $\beta=\gamma=$ 25.0°; see scheme 5 below). In addition, each zwitterion acts as H-donor to an adjacent one (related by the symmetry code $\#1 = i = x,\ -y+1,\ z-1/2$; see Table 2). These latter $-COOH\cdots{}^{-}OOC-$hydrogen bonds and the ring–ring stacking interactions generate a 2D framework with the carboxyl groups toward the external surfaces and stacked pyridyl rings toward the inside (Fig. 2). In the crystal, each water molecule forms two symmetry related and equivalent hydrogen bonds of the type O(1)–H(10)···O(21)#1 (Table 2) toward opposite sides connecting the closest external faces of two adjacent bi-layers (Fig. 2) (Scheme 5).

Since the internal geometry of the ligands could be considered normal (see appropriate refs. for pmda [24–26], pca [21,22] and Hpb [44]), only coordination bond lengths and selected *trans*-angles of (α-picolylamine)(*N*-(2-pyridylmethyl)iminodiacetato)copper(II) thi-hydrate

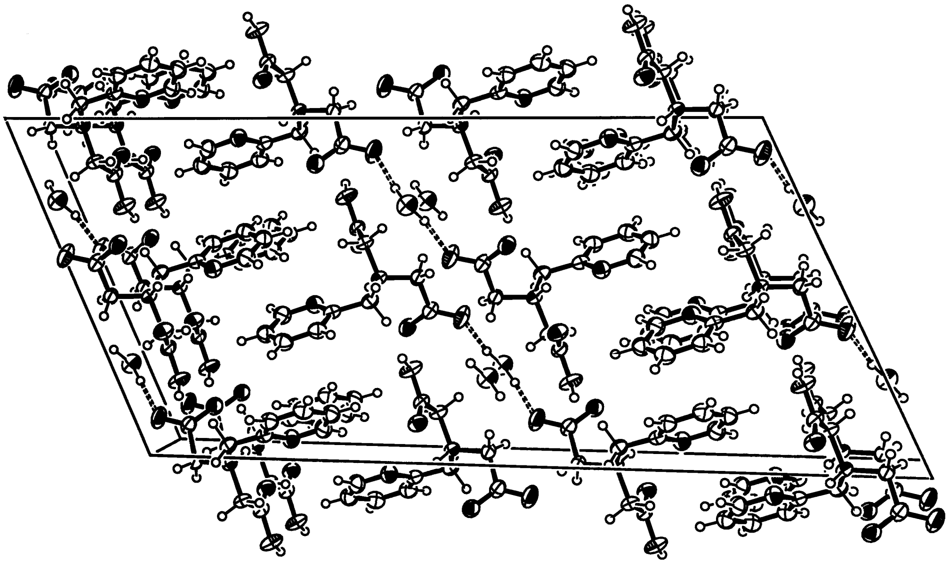


Fig. 2. 2D frameworks of $H_2pmda^{\pm}$ zwitterions and inter-layered connected by the hydrogen bonded water molecules in the unit cell of the acid $H_2pmda\cdot 0.5H_2O$.

Table 3
Copper(II) coordination bond lengths (Å) and *trans*-bond angles (°) in $[Cu(pmda)(pca)]\cdot 3H_2O$ (compound **1**) with e.s.d. in parentheses

Bond lengths			
Cu(1)–O(2)	1.970(2)	Cu(2)–O(24)	1.961(2)
Cu(1)–N(11)	1.993(2)	Cu(2)–N(31)	1.987(2)
Cu(1)–N(16)	2.010(2)	Cu(2)–N(36)	2.019(2)
Cu(1)–N(1)	2.073(2)	Cu(2)–N(2)	2.054(2)
Cu(1)–N(6)	2.418(3)	Cu(2)–N(26)	2.640(3)
Cu(1)–O(4)	2.439(2)	Cu(2)–O(22)	2.359(2)
Bond angles			
N(11)–Cu(1)–N(1)	176.39(1)	N(31)–Cu(2)–N(2)	177.42(1)
O(2)–Cu(1)–N(16)	173.29(1)	O(24)–Cu(2)–N(36)	166.67(1)
N(6)–Cu(1)–O(4)	151.56(8)	O(22)–Cu(2)–N(26)	150.92(8)

Table 4
Copper(II) coordination bond lengths (Å) and *trans*-bond angles (°) in $[Cu(pmda)(Hpb)]\cdot 5H_2O$ (compound **2**) with e.s.d. in parentheses

Bond lengths	
Cu–N(22)	1.970(3)
Cu–O(11)	2.018(2)
Cu–N(11)	2.029(3)
Cu–N(12)	2.032(3)
Cu–O(13)	2.260(3)
Cu–N(21)	2.535(3)
Bond angles	
N(22)–Cu–N(11)	175.75(12)
O(13)–Cu–N(21)	167.44(11)
O(11)–Cu–N(12)	162.56(12)

($[Cu(pmda)(pca)]\cdot 3H_2O$, compound **1**) and (2-(2′-pyridyl)benzimidazole)(*N*-(2-pyridylmethyl)iminodiacetato)copper(II) pentahydrate ($[Cu(pmda)(Hpb)]\cdot 5H_2O$, compound **2**) are listed in Tables 3 and 4, respectively.

The asymmetric unit of compound **1** (Fig. 3) consists of a pair of crystallographically independent molecules [Cu(pmda)(pca)], very similar from a chemical point of view, and six non-coordinated water molecules. Coordination bond lengths (averaged, in Å): Cu–N(aliphatic) 2.064(2), Cu–O(equat.) 1.966(2), Cu–O(apex) 2.399(2) and Cu–N(py ring) 2.529(3) to pmda; Cu–N(py ring) 1.990(2) and Cu–N(primary amino) 2.015(2) to pca ligand. The closest four donors around the copper(II) atom are both N atoms of pca, and the N aliphatic and one O carboxyl atoms of pmda. It is remarkable that the N(pyridyl) and one O carboxyl atom from pmda occupy the apexes of the asymmetrically elongated coordination of copper(II). Two main structural features arise from this structure: (1) the conformational flexibility of the tripodal tetradentate pmda ligand, which occupy two equatorial and two apical coordination sites (instead of three equatorial and an apical ones), and (2) the coordination preference of the *N*(pyridyl)-heterocyclic atom from the secondary pca ligand to occupy the *trans*-position to the Cu–N(aliphatic) bond of pmda.

Compound **2** has one complex molecule and five water molecules in the asymmetric unit (Fig. 4). In this complex, the pmda exhibits a tripodal tetradentate role occupying three equatorial sites and one apical donor site, whereas the *N*,*N*-bidentate Hpb ligand supplies one equatorial atom and one apical donor atom. The structure of the compound **2** shows the preference of the *N*(imidazolyl) donor versus the *N*(pyridyl) donor of

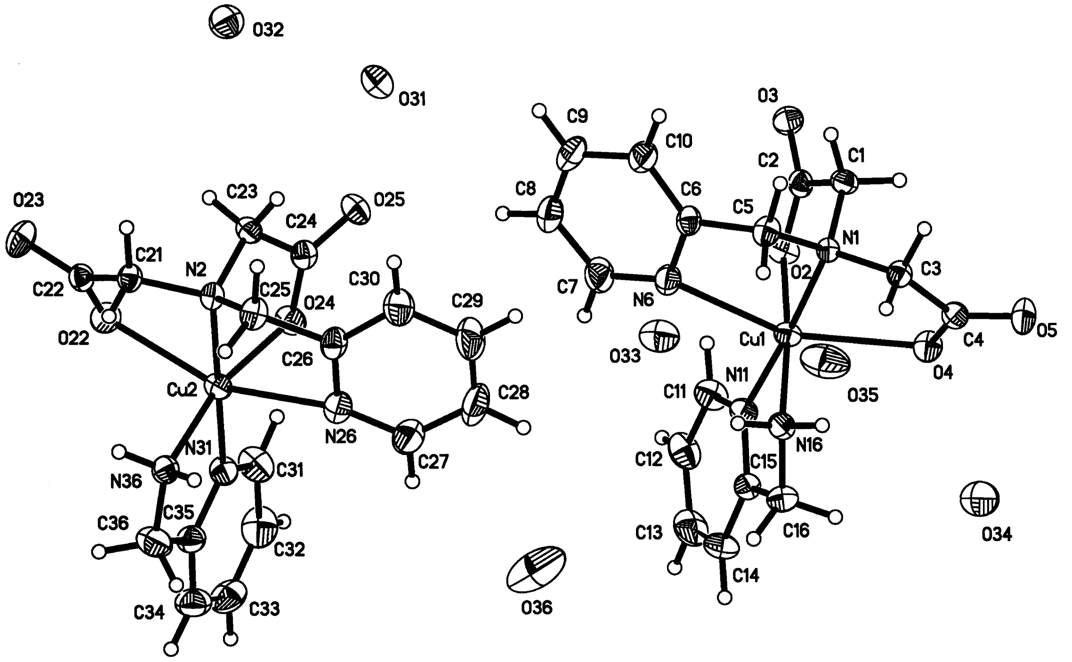


Fig. 3. Asymmetric unit in the crystal of compound **1**, $[Cu(pmda)(pca)]\cdot 3H_2O$, showing the two crystallographically independent complex units and the six independent water molecules.

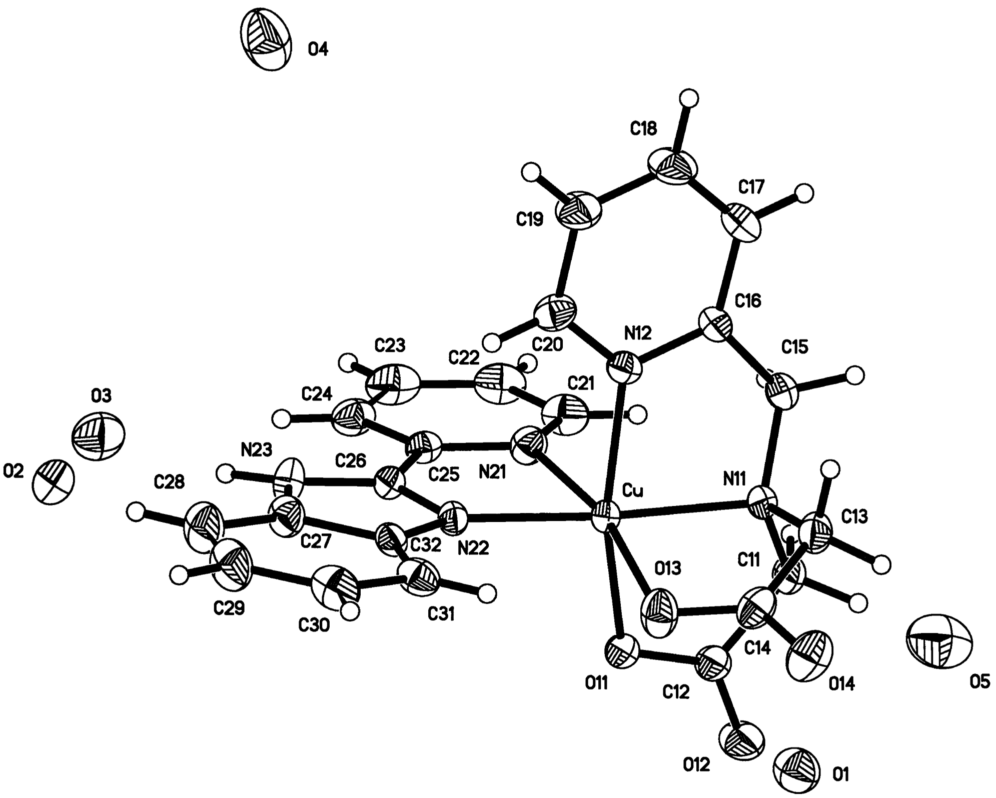


Fig. 4. Asymmetric unit in the crystal of [Cu(pmda)(Hpb)]·$5H_2O$ (compound **2**).

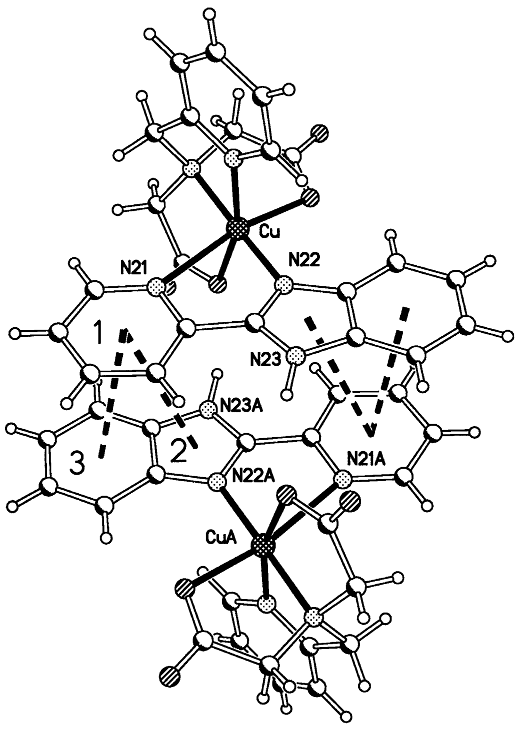


Fig. 5. Aromatic ring–ring π,π-stacking interaction between Hpb ligands of a pair of adjacent molecules in the crystal of [Cu(pmda)(Hpb)]·$5H_2O$ (compound **2**).

Hpb to occupy one among the four closest donor atoms in the distorted octahedral coordination of copper(II) atom; that is just in *trans* to the Cu–N(1) bond of the tertiary amino atom of pmda ligand. In this crystal, pairs of adjacent complex molecules (symmetry related by the code $i = 2-x,\ 1-y,\ z$) have the corresponding Hpb ligands anti-parallel stacked at 3.41 Å (Fig. 5). This π,π-stacking interaction relates approximately the pyridyl ring (ring 1) of each Hpb ligand with the five and six-member rings of the benzimidazolyl moiety from the stacked Hpb ligand (rings 2 and 3, respectively). The analysis of this stacking interaction gives the following structural parameters. Centroid–centroid distances $dc_1-dc_2 = 3.67$ Å and $dc_1-dc_3 = 3.56$ Å. The dihedral angle between stacked rings (α) and angles β and γ of the c–c vector to the normal to the first and second planes (see Scheme 5) are $\alpha = 5.3$, $\beta = 25.6$ and $\gamma = 21.9°$ for planes of rings 1 and 2, and $\alpha = 5.6$, $\beta = 17.2$ and $\gamma = 16.6°$ for planes of rings 1 and 3. The perpendicular distances from the centroid of the ring 1 to the planes 2 and 3 are 3.40 and 3.41 Å, respectively. The perpendicular distances from the centroid of the ring 2 or 3 to the plane of ring 1 are 3.31 and 3.40 Å, respectively. These structural parameters for the stacking between Hpb ligands are consistent with a π,π-interaction with some σ,π-contribution [20]. The crystal is supposedly built linking pairs of complex molecules and water molecules in a hydrogen-bonding array.

In both complexes the copper(II) atom falls in a distorted and asymmetrically elongated octahedral coordination (type 4+1+1), with the four shortest R_S bonds and the two out-of-plane or *trans*-apical longest R_L bonds. In compound **1** there is a remarkable difference in the asymmetry of two molecules, as reflected by the *trans*-apical R_L bond lengths and the tetragonality (T = mean in-plane distance/mean out-of-plane distance) [45] of 0.828 and 0.802 for Cu(1) and Cu(2), respectively. In this complex the individual and the averaged tetragonality (mean $T = 0.815$) falls below that of compound **2** ($T = 0.839$), which has also rather different *trans*-apical R_L bond distances, Cu–O(13) and Cu–N(21). Consequently, the overall elongation of the copper(II) coordination polyhedron is higher in **1** (with lower T) than in **2**.

In the new mixed-ligand Cu(II) complexes, the pmda ligand acts as a tripodal tetradentate as referred in all known structures of complexes with this chelating agent and other metal ions [24–26]. However, the conformation of pmda ligand around the copper(II) in reported chelates is different, because it supplies two equatorial and two apical donors (in **1**) or three equatorial and one axial donors (see above). We found surprising that in compound **1** the rather flexible pca diamine occupies two among the four closest coordination sites around the copper(II) atom, whereas in compound **2** the very rigid Hpb heterocyclic diamine supplies one equatorial and one axial N donors. This apparent controversy can be rationalised considering that both pmda conformations enable the formation of two types of metal-glycinate rings in the complexes studied here. These are the G ring (nearly coplanar to the plane [Cu, N, N] and more strengthened) and the R ring (nearly perpendicular to the plane [Cu, N, N] and less constrained). In the compounds considered here, the G ring falls approximately coplanar with a mean plane P defined by metal and three N donors (two from the pmda ligand and the other from the auxiliary diamine ligand). In contrast, the R ring is roughly perpendicular to the G ring and to the mean plane P of the Cu and three N atoms.

3.2. *Properties of compound* **2**

3.2.1. *Thermal stability*

The TG-DTA diagram of compound **2** showed that the studied compound loses all non-bonded to the metal water molecules in air-dry flow before starting the pyrolytic decomposition (190 °C) of the anhydrous complex (5.469 mg, 10 °C min^{-1}) in two overlapped processes. The infrared spectra of evolved gasses in the first step (190–235 °C) showed a significant production of CO_2, H_2O and N_2O. The lost weight corresponds approximately to the pyrolysis of the pmda–IDA moiety (calc. 27.045%, exp. 28.572%). The second step (235–405 °C) shows the decomposition of remaining organic fragments (with production of CO_2, CO, H_2O and N_2O) to yield CuO (exp. 17.584%, calc. residue 16.539%).

3.2.2. *Electronic and ESR spectra*

The electronic spectrum of **2** shows a d–d band with $\nu_{max} = 13\,320$ cm^{-1} with shoulder at 9000 cm^{-1} and intensity baricenter near 12 500 cm^{-1}. These values are in accordance with a distorted octahedral chromophore CuN_2O_2+N+O (type 4+1+1) [45]. A polycrystalline sample of this compound gives an axial ESR spectrum that is 'reverse' in type ($g_{//} = 2.06 < g_{\perp} = 2.19$) with the lowest g value significantly above 2.00. This behaviour is referred as an antiferrodistortive ordering [45] with total misalignment of the CuN_2O_2+O+N cromophores in the crystal lattice, and is consistent unambiguously with a d_{x2-y2} ground state for the copper(II) atom.

3.2.3. *Magnetic susceptibility*

A plot of χ data versus T(K) (T = 79–290 K) is linear ($1/\chi = (1/C)T - (\theta/C)$ with a statistical r^2 factor of 0.9987) according to a Curie–Weiss behaviour, $\chi = C/(T-\theta)$ [39,45]. The Curie constant is $C = 0.437$ K emu mol^{-1} with Weiss constant of $\theta = 5.45$. The estimated value of μ_{eff} for Cu(II) atom is 1.87 BM. The ESR spectrum and the magnetic susceptibility data are in accordance with the structure reported here and a $Cu\cdots Cu^{ii}$ separation of 7.165(1) Å (symmetry code: ii = $-x$, $1-y$, $-z$).

4. Concluding remarks

From the molecular recognition point of view, it is interesting to note the way in which an inter-molecular hydrogen bond and the pyridyl–pyridyl π,π-stacking interaction co-operate to build the 2D molecular framework of zwitterions in the crystal of $H_2pmda\cdot0.5H_2O$. The pyridyl–pyridyl inter-planar stacking distance in the free acid (3.57(1) Å) is larger than in compounds $\{[Cu(pmda)]\cdot2H_2O\}_n$ (3.19(1) Å) [18b] and [2-(aminomethyl)-pyridine]silver(I) nitrate (3.21(1) Å [22]). It is noteworthy that compounds **1** and **2** do not involve the pmda pyridyl ring in aromatic π,π-stacking forces, whereas compound **2** displays such inter-ligand interactions between adjacent Hpb heterocycles to recognize itself forming pairs of complex units. The most important structural consequence of the insertion of a *N*-(α-pycolyl) arm in the IDA skeleton is an efficient increase of denticity from three (IDA) to four (pmda). In addition, the studied Cu(II) complexes reveal a remarkable conformational flexibility of the tripodal tetradentate pmda ligand. As for the coordination preference for the *trans*-position to the Cu–N(aliphatic) bond, these structures enable to propose the following donor order N(imidazolyl) > N(pyridyl) > N(aliphatic).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 129246 for $H_2pmda \cdot 0.5H_2O$, CCDC No. 172576 for $[Cu(pmda)(pca)] \cdot 3H_2O$ (compound **1**) and CCDC No. 172577 for $[Cu(pmda)(Hpb)] \cdot 5H_2O$ (compound **2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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