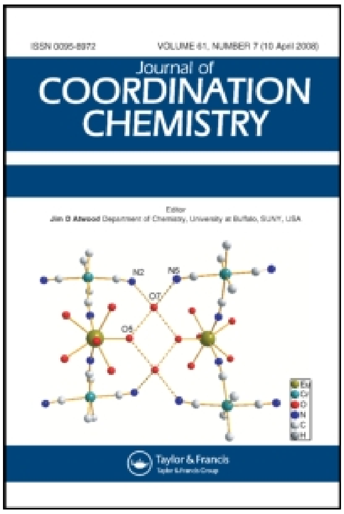

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Synthesis, crystal structure and properties of three different derivatives of bis[di(2-pyridyl)methanediol]copper(II), $[Cu(bpmd)_2]^{2+}$

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Synthesis, crystal structure and properties of three different derivatives of bis[di(2-pyridyl)methanediol]copper(II), $[Cu(bpmd)_2]^{2+}$¶

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In an attempt to obtain ternary copper(II) [Cu(II)] complexes where bis(2-pyridyl) ketone (bpk) could induce the *fac*-$O_2 + N$(apical) conformation in the HL^{2-} form of two different nitrilotriacetates ($HNTA^{2-}$ and $HDNTA^{2-}$), we obtained $[Cu(bpmd)_2][Cu(HNTA)_2] \cdot 2H_2O$ (**1**) and $[Cu(bpmd)_2](H_2DNTA)_2 \cdot 4H_2O$ (**2**) where bpmd is di(2-pyridyl)methanediol. On this basis, the salt $[Cu(bpmd)_2][Cu(IDA)_2] \cdot 6H_2O$ (**3**) [iminodiacetate (IDA) ligand] was also obtained. The crystallographic studies of these compounds revealed that the common cation of these salts results from aquation of bpk in the aqueous media. The aquation of bpk is unexpectedly fast in the case of **1** because crystals appeared on the same day of the synthesis.

Keywords: Copper(II); Di(2-pyridyl)methanediol; Nitrilotriacetate; Iminodiacetato; Crystal structure

1. Introduction

Mixed-ligand complexes have very broad interest in coordination chemistry due to their structures and applications in a variety of fields [1]. Ternary copper(II) [Cu(II)] complexes with iminodiacetates (IDA)-like ligands and *N*-donor auxiliary ligands are a case of study, where conformation of the IDA-moiety depends on the specific IDA derivative and on the number (one or two) of *N*-donor atoms introduced by the *N*-auxiliary ligand (scheme 1).

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¶This article is dedicated to Professor Alfredo Mederos for his contribution to the coordination chemistry.

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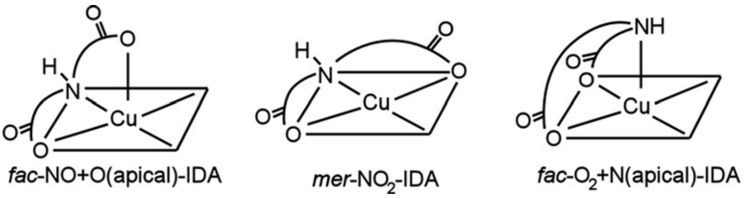
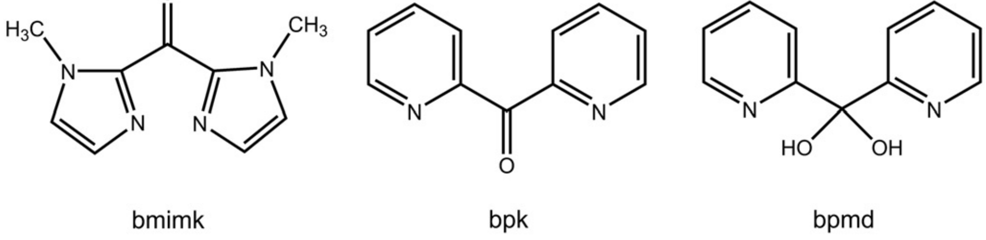
In poly-[Cu(IDA)$(H_2O)_2$] (see [2] and references therein) IDA exhibits a *fac*-NO + O(apical) conformation, unique behavior since the *N*-substituted-IDA ligands give Cu(II) chelates with a *mer*-NO_2 IDA-like conformation [occupying three of the four sites around Cu(II)] [3, 4]. This IDA-conformation is also revealed in a large number of structures for ternary Cu-(IDA-like)-(imidazole-like) complexes and for closely related compounds having a Cu/IDA-like/*N*-donor 1/1/1 ratio (see, e.g. [2c], [3–9]). In clear contrast, compounds with a Cu/IDA/*N*-donor 1/1/2 ratio, such as Cu(IDA-like)$(Him)_2$ [10] or Cu(IDA) (bpy [11] or phen [12]), where Him, bpy or phen are imidazole, 2,2′-bipyridine or 1,10-phenanthroline, respectively, have the IDA moiety in a *fac*-NO + O(apical) conformation, also preferred for the binary Cu-IDA polymer (keeping in mind that the aqua ligands are solvent molecules used to satisfy the metal coordination requirements) (see [2] and references therein). However, related compounds with Cu/IDA-like/*N*-donor 1/1/2 ratio but having *N*-*R*-IDA ligands with a bulky *R* substituent (such as *tert*-butyl [3], adamantyl [4] or *p*-nitro-benzyl [5]) feature a rather unusual *fac*-O_2 + N(apical) IDA conformation, with the *N*-amino-IDA donor displaced to the apical coordination site, far from the metal. In a recent contribution, this family of compounds was extended to [Cu(HNTA)(bmimk)], where bmimk is *bis*(*N*-methylimidazol-2-yl) ketone (scheme 2) [13] with the bidentate bmimk supplying two *N* atoms to Cu(II) and the $HNTA^{2-}$ anion (derived from nitrilotriacetic acid, H_3NTA) a tridentate "*N*-carboxymethyl-IDA ligand", with a free acetic arm and a *fac*-O_2 + N(apical) conformation. The formation of this complex is possible because of the absence of effective protonation sites in the bmink ligand. We have considered the possibility to obtain similar compounds with *bis*(2-pyridyl) ketone (bpk) instead of bmimk (scheme 2); the crystal structure of the ternary compounds $[Cu(bpk)(NO_3)_2]_n$ [14] and $[Cu(bpk)Cl_2]_n$ [15] are known.

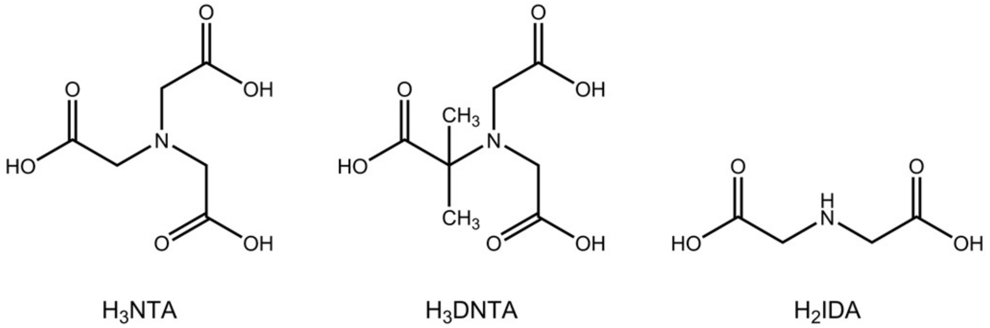
We have used as IDA-like chelating agents the HL^{2-} ions of H_3NTA and H_3DNTA (C, C-dimethylnitrilotriacetic acid) and IDA (scheme 3).



Scheme 1. IDA-like conformations in Cu(II) chelates.



Scheme 2. Bis(2-pyridyl) ketone and relates N_2-ligands.



Scheme 3. Amino-polycarboxylic acids.

2. Experimental

2.1. *Materials and instrumentation*

The C,C-dimethylnitrilotriacetic acid (H_3DNTA) was prepared by reaction of 2-methyl-α-alanine (Merck) and potassium 2-chloroacetate (Merck) in alkaline medium (KOH) as described [16] with a small modification consisting of the separation of a significant amount of KCl (by-product) by several cycles of concentration–cooling–filtration of the neutralized mother liquors, prior to precipitation of the desired product from the acidified solution (pH 2–2.5). All other materials of reagent grade were used as received from Aldrich ($Cu_2CO_3(OH)_2$ malachite), Sigma (H_2IDA), Acros (bpk), or Carlo Erba (H_3NTA). Analytical data were obtained in a Fisons–Carlo Erba EA 1108 elemental micro-analyzer. TG analyses (pyrolysis) of the compounds (295–800°C) were carried out in air flow ($100\,\mathrm{mL\,min^{-1}}$) by a Shimadzu Thermobalance TGA-DTG-50H instrument, and a series of FT-IR spectra (20–30 per sample) of evolved gasses were recorded using a coupled FT-IR Nicolet Magma 550 spectrometer. Infrared spectra were recorded using KBr pellets on a Jasco FT-IR 410 spectrometer. Electronic (diffuse reflectance) spectra were obtained in a Varian Cary-5E spectrophotometer. Electron spin resonance spectra were recorded in X band at room temperature in a Bruker ERP 300E spectrometer.

2.2. *Synthesis of the Cu(II) compounds*

The studied compounds were obtained by the same general procedure. In a Kitasato flask, malachite (1 mmol, 0.22 g) and the appropriate acid (2 mmol, 0.38 g of H_3NTA, 0.44 g of H_3DNTA or 0.26 g of H_2IDA, for $[Cu(bpmd)_2][Cu(HNTA)_2]\cdot H_2O$ (**1**), $[Cu(bpmd)_2](H_2DNTA)_2\cdot 4H_2O$ (**2**) or $[Cu(bpmd)_2][Cu(IDA)_2]\cdot 6H_2O$ (**3**), respectively) were reacted in 100 mL (compounds **1** and **2**) or 200 mL (compound **3**) of distilled water, with smooth heating (<50°C), continuous stirring and vacuum (water pump) until the production of CO_2 (by-product) ceased and all products were dissolved. The resulting blue solutions were cooled to room temperature and, after that, bpk (2 mmol, 0.37 g) was added and dissolved by stirring. The blue-violet solutions were filtered without vacuum on appropriate crystallization devices and left to evaporate at room temperature. Suitable crystals of the product were obtained from one day to several weeks, controlling the evaporation rate with the aid of plastic film covering the crystallization devices. In an independent synthesis of **1**, the crystallization device with the mother solution was placed carefully into a big crystallizing flask which contained acetone, well covered with a paraffin paper, in order to permit diffusion of acetone vapors inside the complex solution, following the procedure reported for synthesis of [Cu(HNTA)(bmimk)] [13]. After 1 day, many well-shaped crystals, suitable for X-ray diffraction studies, were obtained. Yields (%): 87 (**1**), 44 (**2**) and 77 (**3**). Anal. data (%) are as follows. Calcd for **1**: C, 43.18, H, 4.05, N, 8.89; found: C, 43.16, H, 3.84, N, 9.17. Calcd for **2**: C, 46.74, H, 5.37, N, 8.61; found: C, 46.68, H, 5.24, N, 8.65. Calcd for **3**: C, 39.96, H, 4.69, N, 9.32; found: C, 40.06, H, 4.64, N, 9.15.

2.3. *X-ray crystallography*

Suitable crystals were mounted on glass fiber and used for data collection. Data were collected with Bruker SMART CCD 1000 (**1**), Bruker X8 Proteum (**2**) or Bruker Kappa APEX II (**3**) diffractometers at 100(2) K. The data were processed with SAINT (**1**) [17] or APEX2 (**2** and **3**) [18] and corrected for absorption using SADABS [19]. The structures were solved by direct methods [20], revealing positions of all non-hydrogen atoms. These atoms were refined on F^2 by a full matrix least-squares procedure using anisotropic displacement parameters [21]. All hydrogens were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times those of the respective atom. Atom scattering factors were taken from the International Tables for Crystallography [22]. Geometric calculations and molecular graphics were performed with PLATON [23]. Table 1 shows crystal data and solution structure parameters of the three compounds.

Table 1. Crystal data and structure determination details for **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_{34}H_{38}Cu_2N_6O_{18}$	$C_{38}H_{52}CuN_6O_{20}$	$C_{30}H_{42}Cu_2N_6O_{18}$
Formula weight	945.78	976.40	901.78
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)			
a	8.1345(2)	7.9600(11)	14.848(3)
b	17.1009(4)	10.1090(14)	8.2919(15)
c	13.9346(3)	13.4280(19)	16.215(3)
α	90	83.910(3)	90
β	97.9830(10)	79.632(4)	113.553(3)
γ	90	83.760(4)	90
Volume (Å^3)	1919.62(8)	1052.4(3)	1830.0(6)
Z, calculated density (Mg m^{-3})	2, 1.636	1, 1541	2, 1637
Data/parameters	7298/274	2987/297	3745/256
Goodness-of-fit on F^2	1.098	1.046	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0469$ $wR_2 = 0.1403$	$R_1 = 0.0363$ $wR_2 = 0.0949$	$R_1 = 0.0346$ $wR_2 = 0.0832$
R indices (all data)	$R_1 = 0.0651$ $wR_2 = 0.1483$	$R_1 = 0.0366$ $wR_2 = 0.0958$	$R_1 = 0.0580$ $wR_2 = 0.0903$

3. Results and discussion

3.1. *Synthesis*

The stoichiometric reactions of the amino-polycarboxylic acids with basic Cu(II) carbonates are useful procedures to obtain Cu(II) chelates because they give water (the solvent) and CO_2 (as by-product) which is easily removed with the aid of stirring, heating and vacuum. Blue $Cu_2CO_3(OH)_2$ powder or green malachite can be used to this purpose. If the time of reaction is not large enough, the bluish product tends to leave small amounts of CuO residue, which is removed on the filtration device. The malachite reacts slower than the bluish copper hydroxyl-carbonate and does not afford CuO by-product, but a small amount of malachite can be separated in the filtration if the reaction time is insufficient. In general, these strategies of synthesis ensure good yields and, in the millimole range of reactants, provide enough quality and yield of product for structural and physico-chemical study. In the preparation of **2**, the low yield is due to the observation of two different crystals, dark blue-violet crystals, described as **2**, and purple-violet crystals, which, until now, were not suitable for X-ray diffraction studies. These products co-crystallize during the evaporation of half of the solution volume.

3.2. *Crystal structures*

A surprise in this work arose when the crystal structure of **1** revealed that it was a salt of formula $[Cu(bpmd)_2][Cu(HNTA)_2]\cdot H_2O$ (figure 1) instead of the desired ternary compound. In the centro-symmetric cation, Cu(II) is chelated by two bis-(2-pyridyl)methanediol ligands (bpmd, scheme 2) in *fac*-conformation, with an elongated octahedral coordination where the longest Cu–O(alcohol) bond distance is 2.3713(14) Å (table 2). The anion $[Cu(HNTA)_2]^{2-}$ has symmetrical elongated coordination also, type

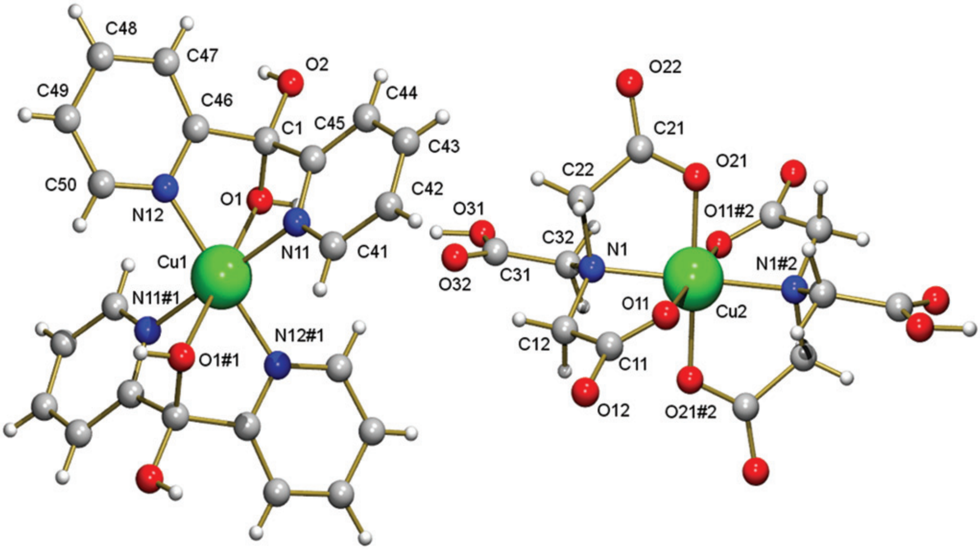


Figure 1. Asymmetric unit of $[Cu(bpmd)_2][Cu(HNTA)_2]\cdot 2H_2O$ (**1**) with the atom-numbering scheme. Water molecules are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2**, and **3**.

		1	**2**	**3**
$[Cu(bpmd)_2]^{2+}$ cation	Cu–O(alcohol)	Cu1–O1 2.3713(14)	Cu1–O8 2.3949	Cu1–O11 2.3921(17)
	Cu–N(py-1)	Cu1–N12 2.0089(17)	Cu1–N15 2.0282	Cu1–N11 2.015(2)
	Cu–N(py-2)	Cu1–N11 2.0175(16)	Cu1–N1 2.0302	Cu1–N21 2.017(2)
$[Cu(L)_2]^{2-}$ anion	Cu–N(amino)	Cu2–N1 2.0516(16)		Cu2–N1 2.014(2)
	Cu–O(carboxy-1)	Cu2–O21 1.9434(15)		Cu2–O31 1.9347(17)
	Cu–O(carboxy-2)	Cu2–O11 2.3577(15)		Cu2–O21 2.4300(18)
Trans-angles		O1–Cu1–O1#1 180.00	O8–Cu1–O8#1 180.00	O11–Cu1–O11#1 180.00
		N12–Cu1–N12#1 180.00	N15–Cu1–N15#1 180.00	N11–Cu1–N11#1 180.00
		N11–Cu1–N11#1 180.00	N1–Cu1–N1#1 180.00	N21–Cu1–N21#1 180.00
		N1–Cu2–N1#2 180.00		N1–Cu2–N1#2 180.00
		O21–Cu2–O21#2 180.00		O31–Cu2–O31#2 180.00
		O11–Cu2–O11#2 180.00		O21–Cu2–O21#2 180.00
Symmetry code		$\#1 -x+1, -y+1, -z+1$; $\#2 -x, -y, -z+1$	$\#1 -x+2, -y, -z+1$	$\#1 -x, -y+2, -z$; $\#2 -x+1, -y+1, -z$

4 + 2, where the longest bond is 2.3578(15) Å, rather similar to that found in the polymer $\{Na_2[Cu(HNTA)_2]\}_n$ with an apical distance of 2.327 Å [24].

No less surprising was the crystal structure of **2** (figure 2), also a salt $[Cu(bpmd)_2](H_2DNTA)_2 \cdot 4H_2O$ with the same cation as **1** [and the longest Cu–O (alcohol) bond of 2.3949(13) Å, table 2], but where the anion was a diprotonated(1–) form of the C,C-dimethylnitrilotriacetic acid. This H_2DNTA^- anion has an acetic arm, but not an isobutyric acid arm. This anion has a zwitterion structure where the N^+–H moiety builds a rather uncommon trifurcated H-bonding interaction with one *O*-acetate, one O(H)-acetic acid and one *O*-isobutyrate as acceptors.

The structures of **1** and **2** led us to obtain a related compound with the *bis*-(IDA) Cu(II) counter-anion. In this context, **3** was obtained and structurally characterized (figure 3). Compound **3** is a salt closely related to **1** consisting of centro-symmetric ions and non-coordinated water. The anion has a 4 + 2 Cu(II) coordination and is similar to the one reported for $K_2[Cu(IDA)_2] \cdot H_2O$ [25]. The cation of **3** [with a 4 + 2 elongated coordination and the longest Cu–O(alcohol) distance of 2.3922(17) Å, table 2] is similar to those of compounds **1** and **2**.

In the studied compounds, the distortion of the bpmd ligand can be attributed to packing effects. Since the three compounds have the same $[Cu(bpmd)_2]^{2+}$ cation, the observed variation in the dihedral angle between pyridyl rings [67.45(10)° (**1**), 72.68(13)° (**2**) and 66.93(10)° (**3**)] is due to different hydrogen bond modes involving the gem-diol bmpd ligand, the carboxylates and water.

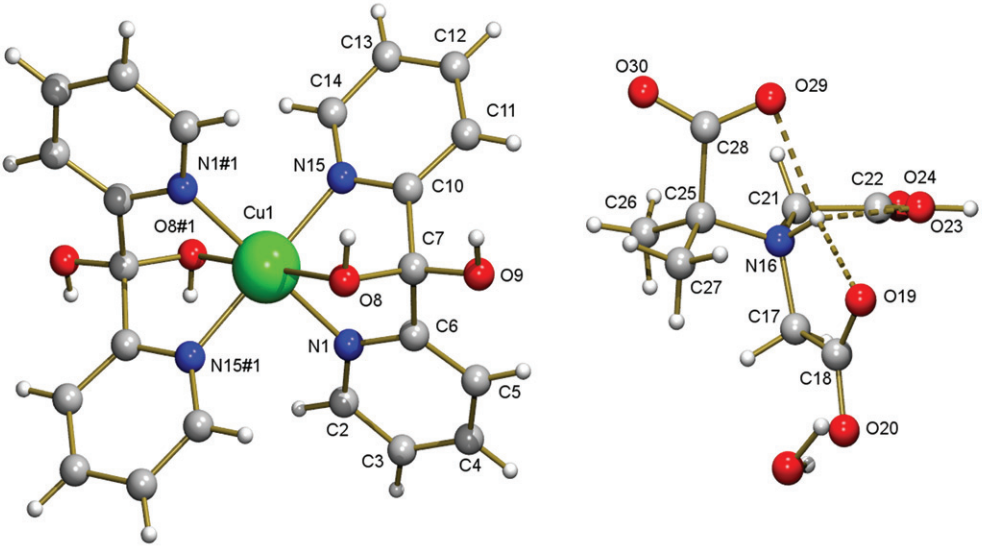


Figure 2. Asymmetric unit of $[Cu(bpmd)_2](H_2DNTA)_2 \cdot 4H_2O$ (**2**) with the atom-numbering scheme. Water molecules are omitted for clarity.

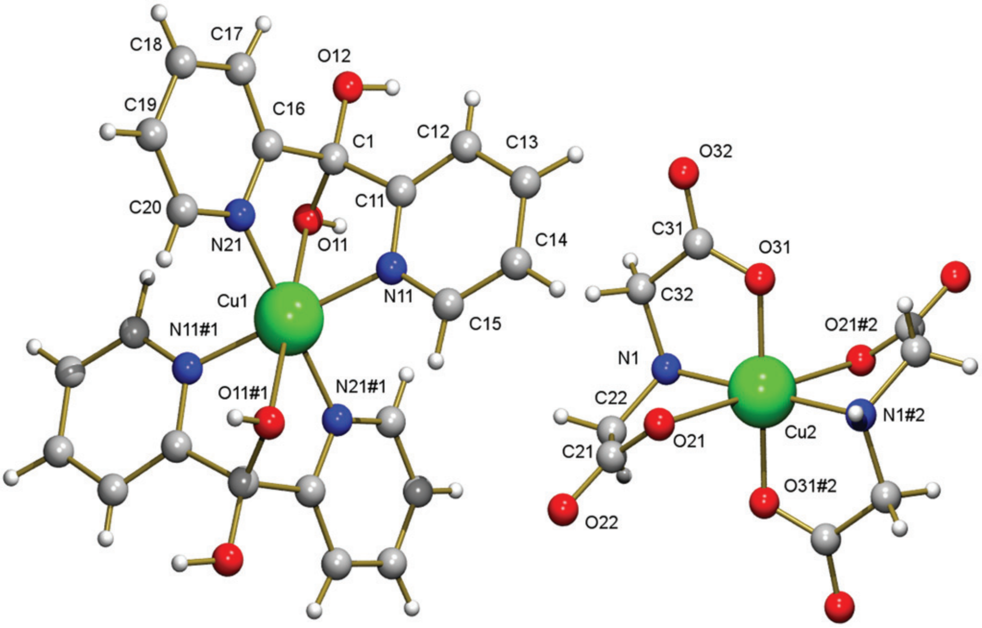


Figure 3. Asymmetric unit of $[Cu(bpmd)_2][Cu(IDA)_2] \cdot 6H_2O$ (**3**) with the atom-numbering scheme. Water molecules are omitted for clarity.

Twelve different Cu(II)-bpmd compounds are in the CSD database. One is the ternary compound $[Cu(NCS)_2(bpmd)]$ [26] [with Cu–O(alcohol) bond of 2.476 Å] and the others are a large variety of salts with the cation $[Cu(bpmd)_2]^{2+}$ and Cu–O(alcohol) bond distances ranging between 2.323 and 2.477 Å [27]. In all these compounds the bpmd ligand is *fac*-tridentate, with the O(alcohol) donor on an apical/distal coordination site. Our compounds provide three new examples of the referred salts. Their formation represents the hydration of the bpk-keto group [28] that is fast in both alkaline and acid aqueous solutions. The rapid formation of crystals of **1** adapting the procedure of synthesis of [Cu(HNTA)(bmimk)] [13] indicates a fast hydration of bpk to give the gem-diol bpmd, in our experimental conditions.

3.3. *Physical properties*

The compounds have no unusual thermal stabilities or spectral properties. However, it should be noted that the IR spectra of the three compounds show, among others, typical defined bands of the "out-of-plane" deformation mode of C–H aromatic bonds, π(C–H), at 813, 805, or 808 and 768, 770, or 765 cm^{-1} for **1**, **2**, and **3**, respectively. These bands have diagnostic values for the presence of bpmd ligand. The spectrum of **1** exhibits ν(O–H) peaks at 3512 and 3475 cm^{-1} of the O–H(carboxylic and alcoholic) chromophores, over the typical broad stretching bands of water. The ν(C=O) and the combination band ν(C–O) + δ(O–H) of carboxylic acids are only observed (cm^{-1}) for **1** (1722s, 1402w) and **2** (1723s, 1408w). In contrast, only the spectrum of **3** exhibits bands of the N–H(IDA) chromophore (ν 3247s and δ 1502vw cm^{-1}). The ν(N–H) band is superimposed to the broad, weak $\nu_s(H_2O)$ band, but the little peak δ(N–H) is easily identified by the absence of bands from other chromophores at these wavenumbers. The spectrum of **3** also suggests two carboxylate chromophores with two absorptions due to the symmetrical stretching mode ν_s(COO), at 1402 and 1388 cm^{-1}, corresponding to the apical and equatorial carboxylate-Cu(II) coordinations in $[Cu(IDA)_2]^{2-}$. The electronic spectra of these compounds are very similar, with an asymmetric d–d band (ν_{max} at 17,330, 17,420, and 17,450 cm^{-1}) and a shoulder near 12,100–12,500 cm^{-1} for **1**, **2**, and **3**, respectively. At room temperature, the ESR spectra of poly-crystalline samples of these compounds are quasi-isotropic, with g_{iso} 2.06 ± 0.01. The electronic and ESR spectra are according to misaligned Cu(II)L_6 chromophores with d_{x2-y2} ground states, as expected for the elongated octahedral Cu(II) coordination (type 4 + 2).

The thermogravimetric behavior consists of water loss followed of pyrolytic steps of the organic ligands to give CuO as a stable residue over 500°C. Compound **1** loses all non coordinated water on the air-dry flow, whereas **2** and **3** retain most water content prior to the pyrolysis of the organic ligands. The pyrolytic steps of the three compounds produce CO_2, CO, H_2O, and *N*-oxides (N_2O, NO, and NO_2) and certain amounts of methanol, acetone or NH_3 and H_2CO. The production of acetone or ammonia from **2** or **3**, respectively, could be related to the presence of the H_2DNTA^{2-} counter-anion of the IDA ligands in such compounds.

4. Concluding remarks

Our results demonstrate that $[Cu(bpmd)_2]^{2+}$ is stable enough to give a variety of salts. Two ideas can be drawn for further works. First, we can attempt to obtain ternary compounds of general formula Cu(Chel)(bpk), where Chel is a chelating(2–) ligand (as IDA, HNTA, or HDNTA), working in polar aprotic solvents or by thermal dehydration of **3** and crystallization in these kind of solvents. Second, we can prepare similar compounds to **2** with H_2NTA^- or $HIDA^-$ as counter-anions or alternatively a compound related to **1** such as $[Cu(bpmd)_2][Cu(HDNTA)_2] \cdot nH_2O$.

Supplementary material

Crystallographic data of compounds $[Cu(bpmd)_2][Cu(HNTA)_2] \cdot 2H_2O$ **1**, $[Cu(bpmd)_2](H_2DNTA)_2 \cdot 4H_2O$ **2** and $[Cu(bpmd)_2][Cu(IDA)_2] \cdot 6H_2O$ **3** have been deposited at the Cambridge Crystallographic Data Centre with CCDC Nos. 691859–691861, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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