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Synthesis, crystal structure and properties of *N*-*tert*-butyliminodiacetic acid (H_2TEBIDA), [Cu(TEBIDA)(H_2O)$_2$], {[Cu(TEBIDA)(Him)]·2H_2O}$_n$, {Cu(TEBIDA) (5MeHim)·H_2O}$_n$, and [Cu(TEBIDA)(2,2′-bipy)(H_2O)]·4.5H_2O, (Him = imidazole, 5MeImH = 5-methylimidazole and 2,2′-bipy = 2,2′-bipyridine)

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Abstract

N-*tert*-butyliminodiacetic acid (H_2TEBIDA, compound **1**) has been prepared and characterised by thermogravimetric analysis, FT-IR and NMR spectra, and X-ray crystallography (final $R_1 = 0.04$). The zwitterion $H_2TEBIDA^{\pm}$ is *intra*-stabilised by a hydrogen bond, and H-bonded chains of zwitterions form supramolecular 2D bilayers with *tert*-Bu groups towards the external faces. Compounds [Cu(TEBIDA)(H_2O)$_2$] (**2**), {[Cu(TEBIDA)(Him)]·2H_2O}$_n$ (**3**) {[Cu(TEBIDA)(5MeHim)]·H_2O}$_n$ (**4**) [Cu(TEBIDA)(bipy)]·4.5H_2O (**5**) were also obtained and studied by thermal, (FT-IR, reflectance and ESR) spectral, magnetic and X-ray diffraction methods. Compound **2** has a molecular structure and TEBIDA with *mer*-NO_2 tridentate conformation in contrast with that reported for {[Cu(IDA)(H_2O)$_2$]}$_n$ (polymeric chains, elongated octahedral Cu(II) coordination and *fac*-NO+O(apical) IDA conformation). Compounds **3** and **4** form zig–zag polymeric chains and follow all structural co-relations reported for complexes with equimolar Cu(II)/iminodiacetato (IDA)/*N*-heterocyclic donor ratio (Cu(II) coordination type 4+1, *mer*-NO_2 TEBIDA conformation and N(Him-like) donor in *trans* to the Cu–IDA-like bond). However, compound **5** has an unexpected *fac*-O_2+N(apical) TEBIDA conformation, with the aqua ligand (instead of one *N*-heterocyclic donor) in the *trans*-site of the Cu–N(IDA-like) bond, in contrast with structural co-relations for complexes with Cu/(IDA or IDA-like)/*N*-heterocyclic donor ratio 1/1/2 and closely related compounds (*fac*-NO+O(apical) IDA-like conformation and one *N*-heterocyclic donor in the *trans*-site to the Cu–N(IDA-like) bond). These findings are attributed to the influence of π,π-stacking interactions involving both rings of two 2,2′-bipy ligands in the molecular recognition process, forming pairs of complex molecules which probably build the crystal of compound **5** with non-coordinated water.

Keywords: Copper(II) complexes; Iminodiacetate; Imidazole; Bipyridine; Crystal structure; Aromatic π,π-stacking

1. Introduction

The structure of *poly*-diaqua(iminodiacetato)copper(II) ({[Cu(IDA)(H_2O)$_2$]}$_n$) [1] and several mixed-ligand copper(II) complexes with IDA and various *N*-heterocycle ligands can serve as 'model compounds' of bio-inorganic interest because of the changes that different secondary ligands of such kind are able to produce in the IDA ligand conformation [1–18]. In this context, the copper(II) chelate is looked at as a metal centre where the IDA or IDA-derivative acts as a protein-like moiety and *N*-heterocyclic donors play roles as substrates or inhibitors. In fact, the structural

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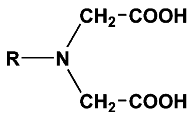
knowledge of these ‘ternary compounds’ has afforded a variety of structural co-relations. For example, IDA (or IDA-like) conformation changes from *fac*- to *mer*- when aqua is replaced in $\{[Cu(IDA)(H_2O)_2]\}_n$ by a mono-dentate *N*-heterocyclic donor ligand, as imidazole (Him) or Him-derivative or a half of 4,4′-bipyridine or pyrazine [1–12]. Subsequently, a change from *mer*- to *fac*-IDA (or IDA-like) conformation is systematically observed going from these 1/1/1 Cu/IDA/*N*-heterocyclic donor compounds to others having a 1/1/2 Cu/IDA/*N*-heterocyclic donor ratio [13–15] or closely related complexes [16–18]. In addition, these latter compounds revealed a preference of the *N*-heterocyclic donor from the secondary ligand for the *trans*-position to the Cu–N(IDA or IDA-like) bond. In this broad context, we become increasingly interested in new mixed-ligand copper(II) complexes having a *N*-R-IDA derivatives with a R chelatable or non-chelatable [10a,10b,12,15,18] aromatic side chain as *primary ligand*, and various *N*-heterocyclic *secondary ligands*. Exploring these possibilities we have found that copper(II) chelates with *N*-alkyl-IDA ligands recognise adenine by its N7 donor atom whereas *N*-benzyl-IDA ligands bind this nucleobase by N3, and with *N*-phenyl-IDA a surprising bridging μ-N3,N7-adenine role was found [11,12].

In order to conclude on the changes in the IDA-like conformations a fundamental insight is, of course, the knowledge of the crystal structure of the copper(II) chelate (without *N*-heterocyclic secondary ligand) which always seems not possible. Now we report a comprehensive series of structural results concerning the *tert*-butyliminodiacetic acid, its copper(II) chelate and three mixed-ligand copper(II) complexes covering a variety of possibilities which enable appropriate structural comparisons.



R	ACID
H	H_2IDA
t-BU	$H_2TEBIDA$

2. Experimental

2.1. Synthesis of $H_2TEBIDA$ acid and copper(II) complexes

TEBIDA ligand was prepared in acid form by reaction of potassium chloroacetate and *tert*-butylamine in alkaline media. In a typical synthesis, 203.55 g of $ClCH_2CO_2H$ (2.154 mol, Aldrich) were dissolved in 300 ml of water and neutralised with 247.33 g of KOH (4.408 mol, Probus) in 100 ml of water, using an ice-salt bath so that the temperature remained below 10 °C, and under N_2 flow. *tert*-butylamine (100 ml, 0.952 mol, Aldrich) was drop-wise added and a water bath (60–70 °C) was used during the condensation reaction (3 h). The reaction mixture was cooled at room temperature and neutralised with HCl 6N. Several cycles of concentration under reduced pressure, cooling with an ice-salt bath and filtration enable the separation (KCl by-product) until significant amount of organic matter was observed when a little amount of the precipitate was burned. Mother liquors were acidified to pH ∼ 2 with HCl 6N and in long standing (several weeks) crude $H_2TEBIDA$ was collected and then recrystallised in water. Suitable crystals for X-ray diffraction studies were grown by a new recrystallisation (2 g of $H_2TEBIDA$ in 50 ml of water). Yield was variable (40–60%, 75–110 g). An alternative synthesis has been reported by Angelici and co-workers [19]. *Anal.* Calc. for $C_8H_{15}NO_4$ (compound **1**): C 50.78, H 7.99, N 7.40, Found: C 50.32, H 8.43, N 7.16. FT-IR relevant frequencies (cm^{-1}): 3433 and 3264 (shoulder) of $\nu(O{-}H)$, 1715 and 1684 of $\nu(C{=}O)$, 1652 of $\nu_{as}(COO)$ in $-COO^{-}\cdots H$, whereas $\nu_s(COO)$ is overlapped with two typical bands expected near of 1385 and 1365 of *tert*-Bu deformation modes [20]. ^1H NMR (300 MHz, D_2O, δ ppm): 0.94 from *tert*-Bu, 2.98 from $N-CH_2-COO$. ^{13}C NMR (75 MHz, D_2O): 25.55 from *tert*-Bu, 55.38 and 55.84 from CH_2, 181.73 from −COO.

Copper(II) complexes were obtained by reaction of $Cu_2CO_3(OH)_2$ (1 mmol) and $H_2TEBIDA$ (2 mmol) in 100 ml of water, under controlled vacuum, stirring and heating with or without the addition of an *N*-heterocyclic ligand (Him, 5MeHim, 2,2′-bipy). The resulting solution was filtered without vacuum on a crystallisation device and evaporated at room temperature. When precipitation initiated, the solution was filtered on another crystallisation device to obtain very well shaped crystals for diffractrometric purposes. Successive samples of these compounds were collected to a yield > 70%. For $[Cu(TEBIDA)(H_2O)_2]$ ($C_8H_{17}CuNO_6$, compound **2**): Calc. C 33.51, H 5.98, N 4.88. Found: 33.56, H 6.37, N 4.95. For $\{[Cu(TEBIDA)(Him)]\cdot 2H_2O\}_n$, ($C_{11}H_{21}CuN_3O_6$, compound **3**): Calc. C 37.23, H 5.97, N 11.92. Found: C 37.48, H 6.23, N 11.92. For $\{[Cu(TEBIDA)(5MeHim)]\cdot H_2O\}_n$ ($C_{12}H_{21}CuN_3O_5$, compound **4**), Calc. C 41.08, H 6.03, N 11.98. Found: C 41.43, H 6.24, N 12.06. For $[Cu(TEBIDA)(2,2'\text{-bipy})(H_2O)]\cdot 4.5H_2O$ ($C_{18}H_{32}CuN_3O_{9.5}$, compound **5**): Calc. C 42.73, H 6.37, N 8.30. Found: C 42.95, H 6.11, N 8.30.

2.2. Crystal structure determinations

A transparent (compound **1**) or a blue (compounds **2**–**5**) prismatic crystal was mounted on a glass fibre and used for data collection. Crystal data was collected at 293(2) K using a Siemens P4 (compounds **1**–**4**) or Bruker SMART CCD 1000 (compound **5**) diffractometer. Graphite monochromated Mo Kα ($\lambda = 0.71073$) radiation was used. The data were processed with the $\omega-2\theta$ scan technique (compounds **1**–**4**) or using SAINT [21] (compound **5**), and corrected for Lorentz and polarisation effects. The data were corrected for absorption using a semi-empirical method (ψ-scans) [22] (compounds **1**–**4**) or using the program SADABS [23] (compound **5**). The structures were solved by direct methods using the program SHELXS-97 [24] and refined by full-matrix least-square techniques on F^2 using SHELXL-97 [25]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps or placed geometrically and positional parameters were refined using a riding model. Atomic scattering factors were obtained from 'International Tables for X-ray Crystallography' [26]. Molecular graphics and geometrical calculations have been obtained from SHELXTL [27] and PLATON [28], respectively. Crystal data for H_2TEBIDA ($C_8H_{15}NO_4$, fw 189.21, 293(2) K): Orthorhombic system, space group $Pna2_1$, $a = 16.356(1)$, $b = 8.384(1)$, $c = 7.044(1)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 965.9(2)$ Å^3, $Z = 4$, $D = 1.301$ Mg m^{-3}, $\mu = 0.104$ mm^{-1}, crystal size $0.6 \times 0.1 \times 0.05$ mm, θ range 2.49°–29.99°, $-1 \leqslant h \leqslant 23$, $-11 \leqslant k \leqslant 1$, $-1 \leqslant l \leqslant 9$, collected/independent reflections 2043/1720, completeness to $\theta = 29.99° = 100\%$, data restraint/parameters 1720/1/129, GOF (on F^2) 1.039, final $R_1 = 0.049$, $wR_2 = 0.1303$ [$I > 2\sigma(I)$], largest difference peak and hole 0.170 and -0.186 e Å^{-3}. A summary of crystal data, experimental details and refinement results for Cu(II)–TEBIDA derivatives (compounds **2**–**5**) are listed in Table 1.

2.3. Physical measurements

All physical measurements were carried out as described in a previous paper [11] excepting that for susceptibility measurement, which were made at room temperature.

3. Results and discussion

3.1. Structure and properties of H_2TEBIDA acid

The internal geometry of H_2TEBIDA has not unusual bond lengths and angles so that appropriate tables could be obtained from the deposited files. The Fig. 1 shows a zwitterion H_2TEBIDA$^{\pm}$, which is the asymmetric unit in the crystal. It is intra-stabilised by only one hydrogen bond N(6)–(H6)···O(3) (2.74(1) Å, 115(3)°) ammonium–carboxylate group. Zwitterions link in translation chains by an hydrogen bond O(10)–H(10)···O(4)^i (symmetry code $i = x, y, z+1$) which is rather short and linear (2.46(1) Å, 171(4)°). Such chains pack in supramolecular 2D structures parallel to the *bc* plane, with the H_2IDA-like moiety inwards and the *tert*-Bu arms towards external faces. These layered structures fall perpendicular to *a* axis in the crystal.

Besides the spectral properties, it should be noted that the pyrolytic decomposition (175–538 °C) of compound **1** shows three steps and initiates by a decarboxylation (step I, 175–210 °C, loss of CO_2) followed by a pyrolytic decarboxylation (step II, 210–280 °C, loss of CO_2, CO, and H_2O). In addition, the last step (280–535 °C) produces a loss of nitrogen products (NH_3, N_2O, NO) and isobutene (IBT).

3.2. Structure of Cu(II)–TEBIDA complexes

Metal–ligand bond distances and angles, structural parameters for distortion of coordination polyhedron and other geometrical data are given in Table 2. Compounds **2**–**4** exhibit a square pyramidal coordination (type 4+1) whereas compound **5** has an elongated octahedral coordination (approaching the type 4+2). Compound **2** has a molecular structure (Fig. 2(a)) and TEBIDA exhibits the *mer*-NO_2 tridentate conformation, with the mean planes of two copper–glycinato chelate rings defining a dihedral angle ϕ of only 9.0(2)°. These features are in clear contrast with the structure of copper(II)–iminodiacetate, $\{[Cu(IDA)(H_2O)_2]\}_n$ [1], a *catena*-polymer, with elongated octahedral coordination and IDA in *fac*-NO+O-tridentate conformation and displaying both chelating and bridging ligand roles. The *mer*-NO_2 tridentate conformation of TEBIDA in its Cu(II) chelate should be related to the steric constraints due to the *N*-*tert*-butyl group on the conformational flexibility of the IDA chelating moiety. Indeed, the *mer*-NO_2-tridentate conformation has been found in eight Cu(II) chelates with *N*-(phenyl-like)iminodiacetato(2−) ligands (without coordinating donor atoms in the substituent of the phenyl ring) [29–36] and in the dinuclear Cu(II) complex unit of ethylenediaminotetraacetate(4−) ion (EDTA), $\{[(H_2O)Cu(EDTA)Cu(H_2O)]\cdot 2H_2O\}_n$ [37]. In this latter compound each Cu(IDA-like) chelate moiety is upon the steric constraints imposed by the 'bulky remain part' of the complex [$-C_2H_4N$(IDA)Cu(H_2O)]. Such steric factor seems to decrease on increasing the poly-methylene chain in EDTA-like ligand, so that in $[(H_2O)Cu(1,6\text{-HDTA})Cu(H_2O)]\cdot 4H_2O$ (1,6-HDTA = hexamethylene-1,6-diaminotetraacetato(4−) ligand) both Cu(IDA-like) moieties exhibit a *fac*-NO+O tridentate conformation comparable to that of IDA in *catena-poly*(diaqua)(iminodiacetato)copper(II) [38]. A *fac*-NO+O IDA-like conformation has also been reported in the copper(II) chelate of *N*-carboxymethyl-L-prolinato(2−) [39]. The conformation of each chelate ring in compound **2** is of the un-symmetrical envelope type (with both C atom unequally displace toward the same side of

Table 1
Crystal data and structure refinement for copper(II)-TEBIDA compounds (**2**–**5**)

Cu(II) compound	**2**	**3**	**4**	**5**
Empirical formula	$C_8H_{17}CuNO_6$	$C_{11}H_{21}CuN_3O_6$	$C_{12}H_{21}CuN_3O_5$	$C_{18}H_{32}CuN_3O_{9.5}$
Formula weight	286.78	354.85	350.86	506.01
Temperature, K	293(2)	273(2)	293(2)	293(2)
Wavelength, λ	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Cmca*	*Pbca*	$P2_1/n$	$P2_1/c$
Unit cell dimensions				
a(Å)	10.732(1)	16.494(1)	9.775(1)	11.328(8)
b(Å)	10.381(7)	7.980(7)	7.853(8)	12.788(9)
c(Å)	21.569(1)	2.805(3)	19.614(3)	16.543(1)
α(°)	90	90	90	90
β(°)	90	90	92.38	93.672(2)
γ(°)	90	90	90	90
Volume (Å^3)	2403.1(4)	3133.45(5)	1504.4(3)	2392(3)
Z	8	8	4	4
Calc. density (Mg m^{-3})	1.585	1.504	1.549	1.405
Absorption coefficient (mm^{-1})	1.830	1.423	1.476	0.966
$F(0\,0\,0)$	1192	1480	732	1064
Crystal size (mm)	0.40 × 0.35 × 0.20	0.40 × 0.35 × 0.06	0.45 × 0.40 × 0.25	0.08 × 0.16 × 0.20
θ Range data collected (°)	1.89–29.99	1.71–27.51	2.08–30.00	1.8–28.14
Index ranges	$-15 \leqslant h \leqslant 1$, $-1 \leqslant k \leqslant 14$, $-1 \leqslant l \leqslant 30$	$-1 \leqslant h \leqslant 21$, $-1 \leqslant k \leqslant 10$, $-30 \leqslant l \leqslant 1$	$-1 \leqslant h \leqslant 13$, $-1 \leqslant k \leqslant 11$, $-27 \leqslant l \leqslant 27$	$-14 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 16$, $-21 \leqslant I \leqslant 16$
Reflections collected/unique	2295/1827 [$R_{int} = 0.0362$]	4564/3596 [$R_{int} = 0.050$]	5767/4389 [$R_{int} = 0.0274$]	11946/5173 [$R_{int} = 0.1345$]
Completeness to θ	29.99°/99.8%	27.51°/99.8%	30°/100%	28.14°/88.5%
Absorption correction	empirical	empirical	empirical	sabads
Max./min. transmission	0.4063/0.3452	0.6913/0.5285	0.5465/0.4739	0.1000/0.438
Refinement method	FMLS[a] on F^2	FMLS[a] on F^2	FMLS[a] on F^2	FMLS[a] on F^2
Data/restraints/parameters	1827/0/98	3596/6/211	4389/0/194	5173/0/289
Goodness-of-fit on F^2	1.080	1.044	1.034	0.759
Final R indicates [$I > 2\sigma(I)$]	$R_1 = 0.038$, $wR_2 = 0.098$	$R_1 = 0.0481$, $wR_2 = 0.098$	$R_1 = 0.039$, $wR_2 = 0.092$	$R_1 = 0.062$, $wR_2 = 0.122$
R indices (all data)	$R_1 = 0.0474$, $wR_2 = 0.106$	$R_1 = 0.100$, $wR_2 = 0.118$	$R_1 = 0.063$, $wR_2 = 0.102$	$R_1 = 0.274$, $wR_2 = 0.161$
Largest difference peak/hole (e Å^{-3})	0.667/−0.636	0.476/−0416	0.392/−0.513	0.396/−0.564

[a] FMLS, full-matrix least-square.

the corresponding NCuO plane). This is the most common chelate ring conformation for Cu-(glycinato-like) rings and in fact is also observed in compounds **3**–**5** of the present study. For symmetry reasons, the molecule of compound **2** has a mirror plane containing the Cu, N(6) and C(18) atoms, as well as the O(2) donor of the closest aqua ligand. This aqua ligand forms two hydrogen bonds of the type O(2)–H(2)···O(10) forming a layer parallel to the *ab* plane at the same time that the apical aqua ligand forms hydrogen bonds of the type O(3)–H(3)···O(10) connecting to such layers in a supramolecular 2D framework which has the *N*-*tert*-butyl arms towards the external faces. Hydrophobic contacts connect these bi-layers perpendicular to the *c* axis (Fig. 2(b)). This packing has notable similarities with that of H_2TEBIDA (compound **1**).

Compounds **3** and **4** (Figs. 3 and 4) have *catena*-polymeric structures because of both chelating and bridging roles of TEBIDA ligand, this latter due to a bridging carboxylate group. The chains extend parallel to the *b* axis. These compounds have typical structural features of those having an equimolar ratio (1/1/1) Cu(II): IDA or IDA-derivative: *N*-heterocyclic donor, such as square base pyramidal coordination (type 4+1) for the copper(II) atom, a *mer*-NO_2-tridentate conformation for IDA-like ligand, and the *N*-heterocyclic donor atom in the *trans*-site to the Cu–N(IDA-like) bond, both among the four closest donor atoms of the metal surrounding.

Data of Table 2 also show differences in the tetragonality T (ratio between the mean of the four shortest and largest distances), the distortion of the square base pyramidal ($\tau = 0\%$) towards bipyramidal coordination ($\tau = 100\%$) and other structural parameters. It can be appreciated that there is a correlation between the Cu–O(apical) distance and the tetragonality in the order **2** < **4** < **3**, but other data seem capriciously disappointed due probably to the influence of crystal packing. However, it should be noted that the presence of Him (in **3**) or 5MeHim (in **4**) represents a significant lengthening of the Cu–O(carboxyl) bonds and an opening of the ϕ dihedral angle between the mean chelate rings in comparison with the values of compound **2**. It is also evident that, as expected, the 4/5-methylimidazole is

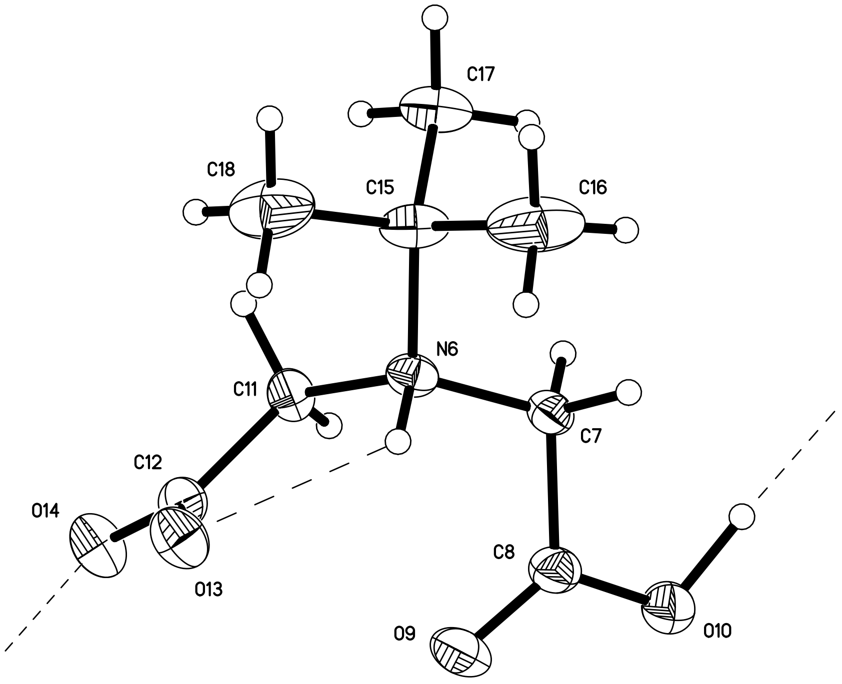


Fig. 1. Zwitterionic structure of H_2TEBIDA acid (compound **1**; dotted lines indicate hydrogen bonding interactions).

linked to the copper(II) as 5-methylimidazole (compound **4**), producing the 'remote isomer' with lower steric constraints than in the hypothetical 'adjacent isomer' (with 4MeHim). The influence of the steric factor is also observed comparing the values of the ε (dihedral angle between Him-like and $P-1$ mean basal planes) and δ (distance of the copper(II) to the heterocycle plane), data which are in the order **3** < **4**. As far as concerns to the crystal packing, the zig–zag chains of the compounds **3** and **4** are cross-linked in 2D sheets by of N–H···O(carboxyl) bond connecting pairs of Him-like ligands of different chains. These 2D sheets are hydrogen bonding connected in a 3D network involving non-coordinated water molecules.

Compound **5** (Fig. 5(a)) consists in [Cu(TEBIDA)(2,2′-bipy)(H_2O)] molecules and four and a half water molecules (because of the special atomic coordinates of O(15) atom). The copper(II)

Table 2
Coordination bond distances in compounds **2**–**5** and parameters for the distortion of their copper(II) coordination polyhedron

	2	3	4	5
Cu–Ow(1)	1.956(2)	–	–	–
Cu–N(hc)	–	1954(3)	1967(2)	2.009(5)
Cu–N′(hc)	–	–	–	2.017(5)
Cu–O(carboxyl)	1.918(2)	1.947(2)	1.953(2)	1.948(4)
Cu–O(carboxyl)	1.918(2)	1.9508(2)	1.959(2)	1.975(5)
Cu–N	2.042(2)	2.040(3)	2.032(2)	2.483(6)
Cu–Ow(2)	2.311(3)	–	–	2.512(5)
Cu–O(carboxyl)	–	2.427(3)	2.341(2)	–
Cu–Cu	6.597	5.521	6.091	7.703
τ (%)	23.53	16.45	25.07	–
T	0.85	0.81	0.84	0.80
ρ(Cu/$P-1$)*	0.27(1)	0.15(1)	0.20	$0.076_{\text{(N-TEBIDA)}}$
ϕ	9.0(2)	20.4(2)	19.9(2)	78.6(2)
TEBIDA conformation	*mer*-NO_2	*mer*-NO_2	*mer*-NO_2	*fac*-$O_2+N_{\text{(apex)}}$
$\varepsilon(P\bar{1}$/hc)	–	16.7	24.6	5.7
δ(Cu/hc)	–	0.22	0.32	0.054
Symmetry codes**	(1) $-x+1,y,z$	(1) $-x+3/2$, $y+1/2$, z (2) $-x+3/2$, $y-1/2$, z	(1) $-x+3/2$, $y-1/2$, $z+1/2$ (2) $-x+3/2$, $y+1/2$, $z+1/2$	

*Deviation towards N(TEBIDA) apical donor atom. **Adjacent Cu atoms falls as indicate the corresponding symmetry code (at the bottom of this table).

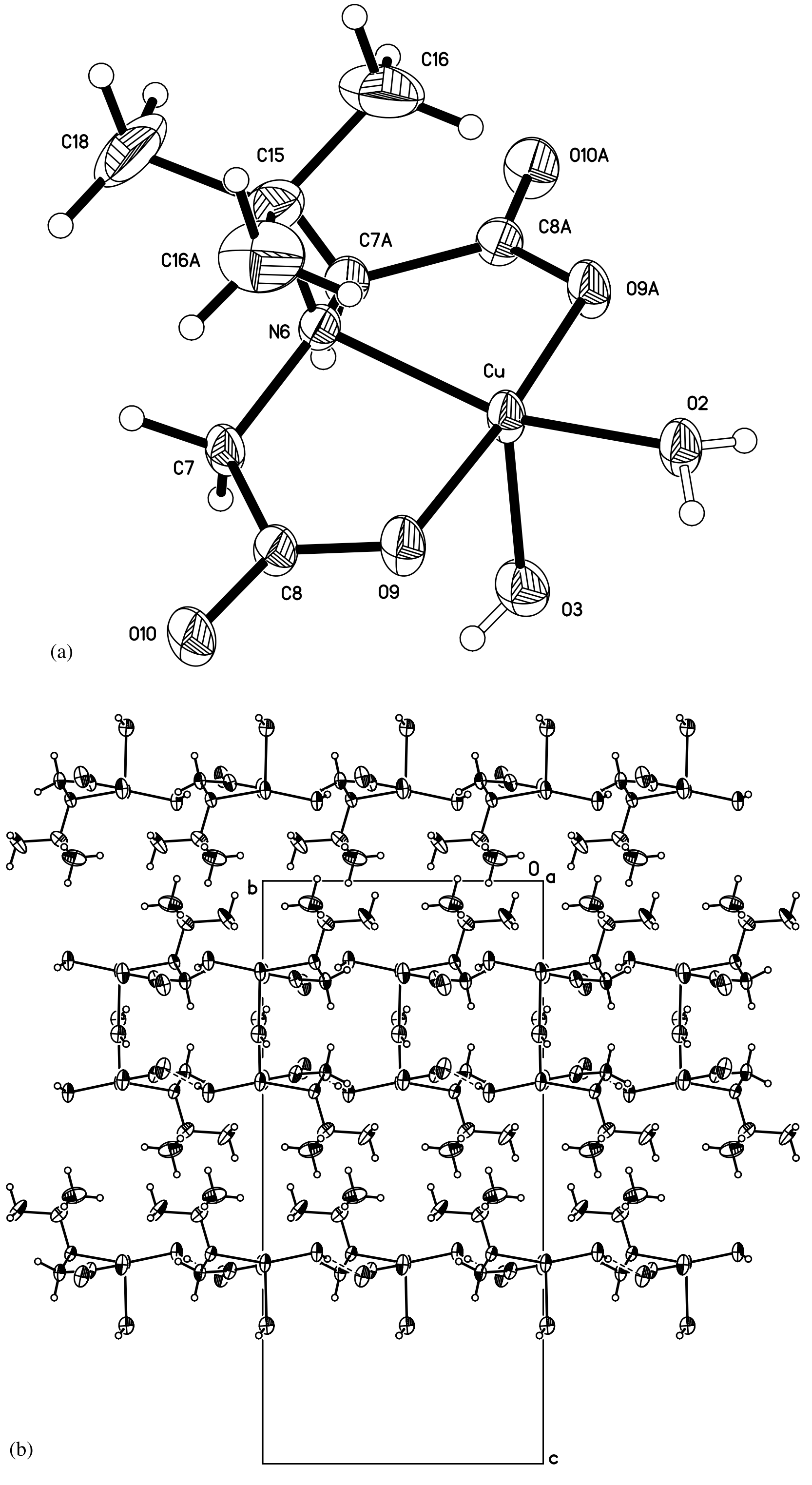


Fig. 2. (a) Molecular structure of [Cu(TEBIDA)(H_2O)$_2$] (compound **2**). (b) Hydrophobic interactions of *N*-*tert*-butyl groups at the external surfaces in a 2D framework of compound **2** connecting with these groups at one face of two adjacent bilayer (up and down).

atom exhibits an unsymmetrical elongated coordination type 4+1+1 (close to type 4+2). The distortion of the coordination polyhedron also concerns the *trans*-angles, which are unequal and lower than 180°: N(1)–Cu–O(5) (153.2°) < O(3)–Cu–N(12) (169.4°) < O(1)–Cu–N(11) (170°). The reason for such important distortion seems the unexpected *fac*-O_2+N(apical) tridentate TEBIDA conformation, which is without doubt the most striking structural feature of this compound. That is in contrast with the *fac*-NO+O(apical)-tridentate IDA in {[Cu(I-

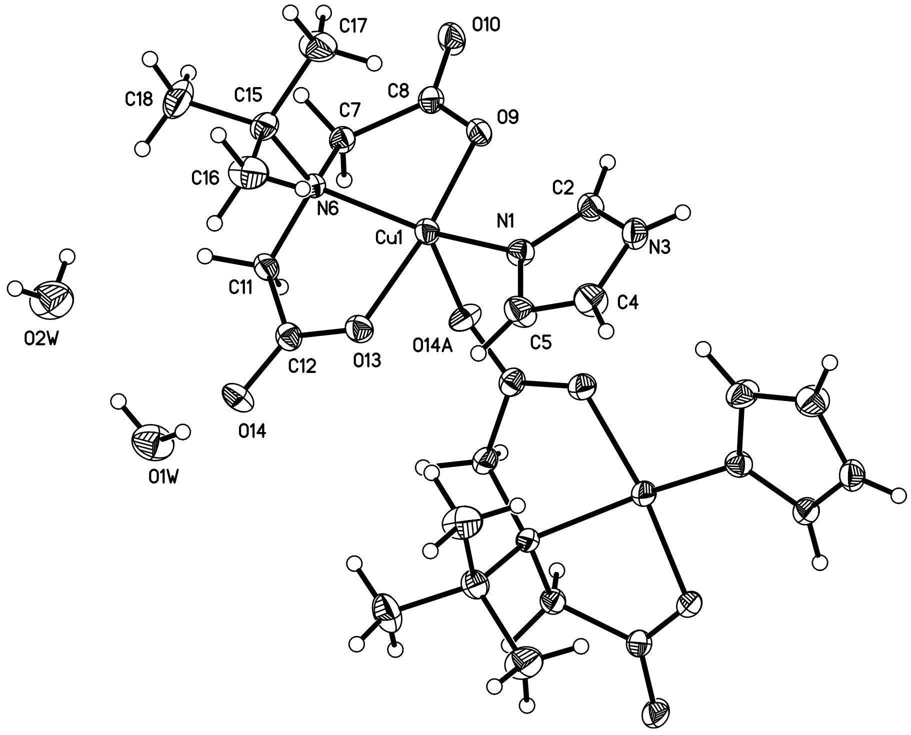


Fig. 3. Fragment of a chain of {[Cu(TEBIDA)(Him)]·$2H_2O$} (compound **3**).

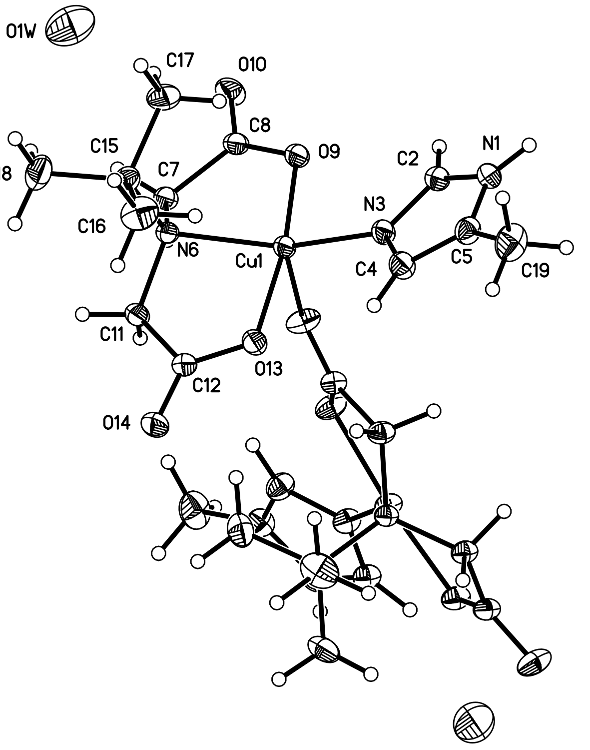


Fig. 4. Fragment of a chain of {[Cu(TEBIDA)(5MeHim)]·H_2O} (compound **4**).

DA)(H_2O)$_2$]}$_n$ [1] and [Cu(IDA)(2,2′-bipy)]·$6H_2O$ [14b] and in closely related compounds [16–18] having a molar ratio Cu(II)/IDA or IDA-like/*N*-heterocycle donor 1/1/2. The dihedral angle between the Cu-glycinato-like chelate rings in compound **5** is 78.6(2)° (versus 82.35° in the Cu–IDA chelate 1a and 78.15° (average) in the ternary Cu/IDA/2,2′-bipy derivative). A *fac*-O_2+ N(apical) conformation of TEBIDA in compound **5** could be attribute to the remarkable π,π-stacking interaction involving the two pyridine-like rings of 2,2′-bipy ligands of pairs of molecules (Fig. 5(b)). These stacking interactions, recently reviewed by Janiak [40], connect two molecules of compound **5** symmetry related by an inversion centre (symmetry code $i = 1-x, 2-y, 2-z$). Each ring–ring stacked pair of 2,2′-bipy ligands defines an inter-planar dihedral angle α of 4.71° and slipping angles β and γ [40] of 20.27° and 24.95°, respectively. The centroid–centroid distance for two pyridine-like stacked rings is 3.78 Å, and the averaged stacking distance $d_{\pi-\pi}$ is 3.5(1) Å. It is noteworthy that TEBIDA ligand is also able to adopt a *fac*-NO+ O(apex) conformation as indeed occurs in the bis-chelate anion of K[Cr(TEBIDA)$_2$]·$4H_2O$ [41], the unique crystal structure reported previously for TEBIDA. In addition, compound **5** differs from typical complexes having a Cu(II)/IDA or IDA-like/*N*-heterocyclic donor ratio 1/1/2 in that the *trans*-site of the Cu–N(TEBIDA) bond is occupied by the apical aqua ligand (and not for one *N*-heterocyclic donor).

In order to rationalise the unexpected structural features of compound **5** it is instructive to consider the two possible TEBIDA conformations in a copper(II) complexes also having a 2,2′-bipy ligand. These TE-

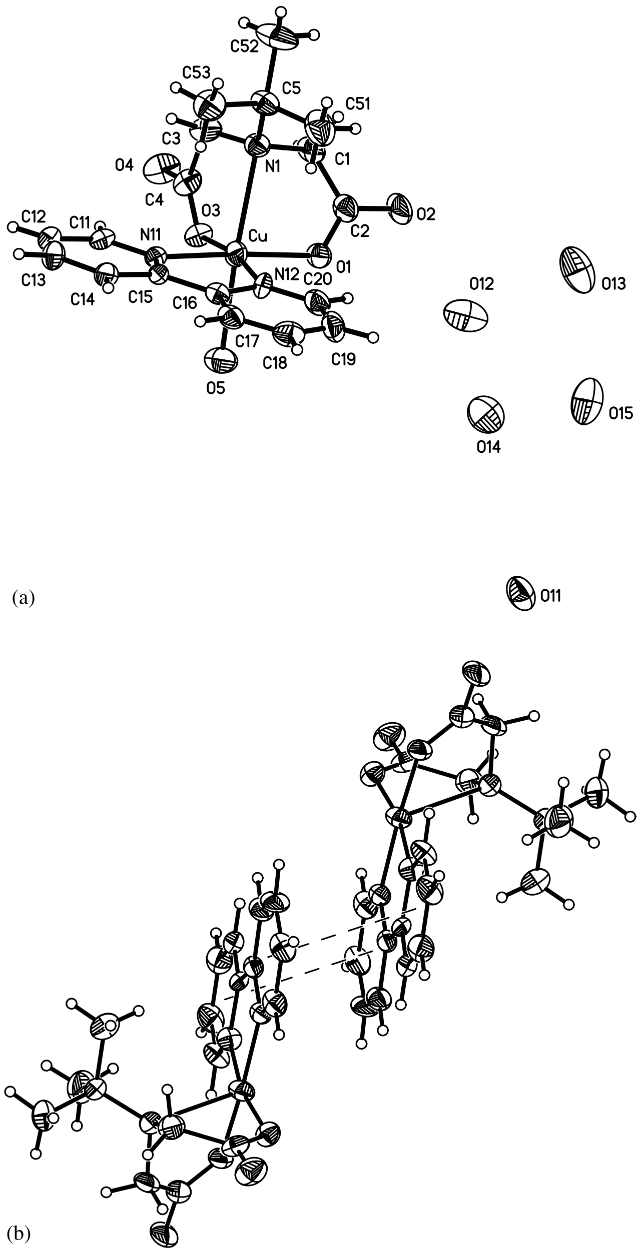
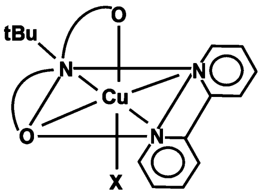
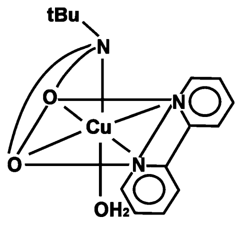


Fig. 5. (a) Asymmetric unit in the crystal of [Cu(TEBIDA)(2,2′-bipy)(H_2O)]·4.5H_2O (compound **5**; H atoms of water molecules omitted). (b) π,π-stacking interactions between both pyridyl rings of a pair of complex molecules of compound **5**. Dotted lines represent centroid–centroid segments of the stacked aromatic rings.

BIDA conformations are *fac*-NO+O(apical) (Scheme 1) and *fac*-O_2+N(apical) (Scheme 2). We can appreciate that in Scheme 1 the Cu–N(heterocyclic) bonds have different (N or O) donor atoms in *trans*-sites to the N(2,2′-bipy) donors, whereas in Scheme 2 there is 2 equiv. O(carboxyl) donor atoms occupying such *trans*-sites. It seems clear that this latter form is chosen to enable a molecular recognition pattern in which the two pyridyl rings of a pair of 2,2′-bipy ligands display a π,π-stacking interactions, as indeed is observed in the structure of compound **5**. Otherwise, it should be noted



Scheme 1.



Scheme 2.

that 2,2′-bipy forms a dihedral angle of 5.7° with the mean plane $P\bar{1}$ of the four closest donors of the Cu(II) atom, which is displaced 0.076 Å toward the apical

Table 3
Summary of thermal, spectral and magnetic properties of Cu(II) compounds **2**–**5**

Compound	**2**	**3**	**4**	**5**
TG analysis				
H_2O in formula	2	2	1	5.5
H_2O on starting TG	1.93	1.17	0.21	0.9
No. Steps	2	4	5	3
Temperature (°C)	70–410	25–430	110–440	20–430
Loss in 1st step	H_2O	H_2O	H_2O	H_2O
Others steps loss	IBT+X [a]	IBT+X [a]	IBT+X [a]	X [a]
Final residue	CuO	CuO	CuO	CuO
IR spectrum (cm^{-1})				
H_2O ν_{as}	3391	3421	3465	3410
δ	1686	1620	1649	1608
Him ν(NH)	–	3201, 3161	3233	–
δ(N–H)	–	1545	1510	–
Carboxylate ν_{as}	1598	1586	1608	1608
ν_s [b]	1400	1377	1399	1371
Electronic spectrum				
ν_{max} (cm^{-1})	13 930	14 800	14 325	15 000
$\nu_{baricenter}$ (cm^{-1})	12 800	14 100	13 215	10 535
ESR spectrum				
Type	axial	axial	quasi-iso	axial
$g_{\parallel}$	2.27	2.22	–	2.29
$g_{\perp}$	2.04	2.06	–	2.05
$g_{average}$	–	–	2.13	–
Magnetic properties (293 K)				
μ (B.M.)	1.73	1.83	1.87	1.89

[a] Other gasses: H_2O, CO_2, CO and NH_3 and/or NO and/or N_2O.

[b] This band is influenced by typical absorptions of *tert*-Bu deformation modes expected near 1385 and 1365 cm^{-1}.

N(TEBIDA) donor. The metal is very close to the 2,2′-bipy plane (0.054 Å).

Table 3 summarises data of the thermal, spectral and magnetic properties of Cu–TEBIDA derivatives, which are in good agreement with the structure of the studied compounds. It is remarkable that compounds **2**–**4** (as well as H_2TEBIDA acid) pyrolyse with production of isobutene (IBT, 2-methylpropene) as a gas typically produced from TEBIDA. A selection of FT-IR spectra of evolved gasses during relevant moments of TG-analysis for compound **4** is shown in Fig. 6. The production of IBU is not observed for compound **5** as it should be expected for the second step (150°–275°) which is fast and important enough (72.5% of weight loss) to enable the formation of this alkene instead of more thermodynamically stable by-products as CO_2 and H_2O. Such a fast pyrolytic behaviour is currently observed for Cu-2,2′-bipy complexes.

The infrared spectra of the studied compounds show evident bands for the stretching modes of water and carboxylate groups. In addition, compounds **3** and **4** exhibit stretching and bending absorptions of the N–H imidazolic bonds. The maximum intensity of the d–d band increases the series of Cu–TEBIDA chelates with aqua, imidazole and 2,2′-bipy as auxiliary ligands. For five-coordinated complexes, the intensity baricenter of the imidazole-containing complexes is higher than that of the *N*-heterocycle free Cu–TEBIDA chelate. ESR spectra of the studied complexes are of axial or quasi-isotropic types with the lowest *g* value significantly over 2.03 in accordance with the misalignment of the chromophores of the studied complexes in their crystal lattices. These spectra are also consistent with a $d_{x^2-y^2}$ ground state for the copper(II) as should be expected for the elongated square base pyramidal (compounds **2**–**4**) or octahedral (**5**) coordination polyhedron. The effective magnetic moments are typical for dilute magnetic Cu(II) complexes with large Cu(II)–Cu(II) separations. They vary from the spin-only value of **1** to others higher values in the range of 1.8–2.0, probably due to mixing-in of some orbital angular momentum from excited states via spin-orbit coupling.

4. Concluding remarks

Our results show that *N*-*tert*-butyl substituent displays its hydrophobic character in the crystal structure

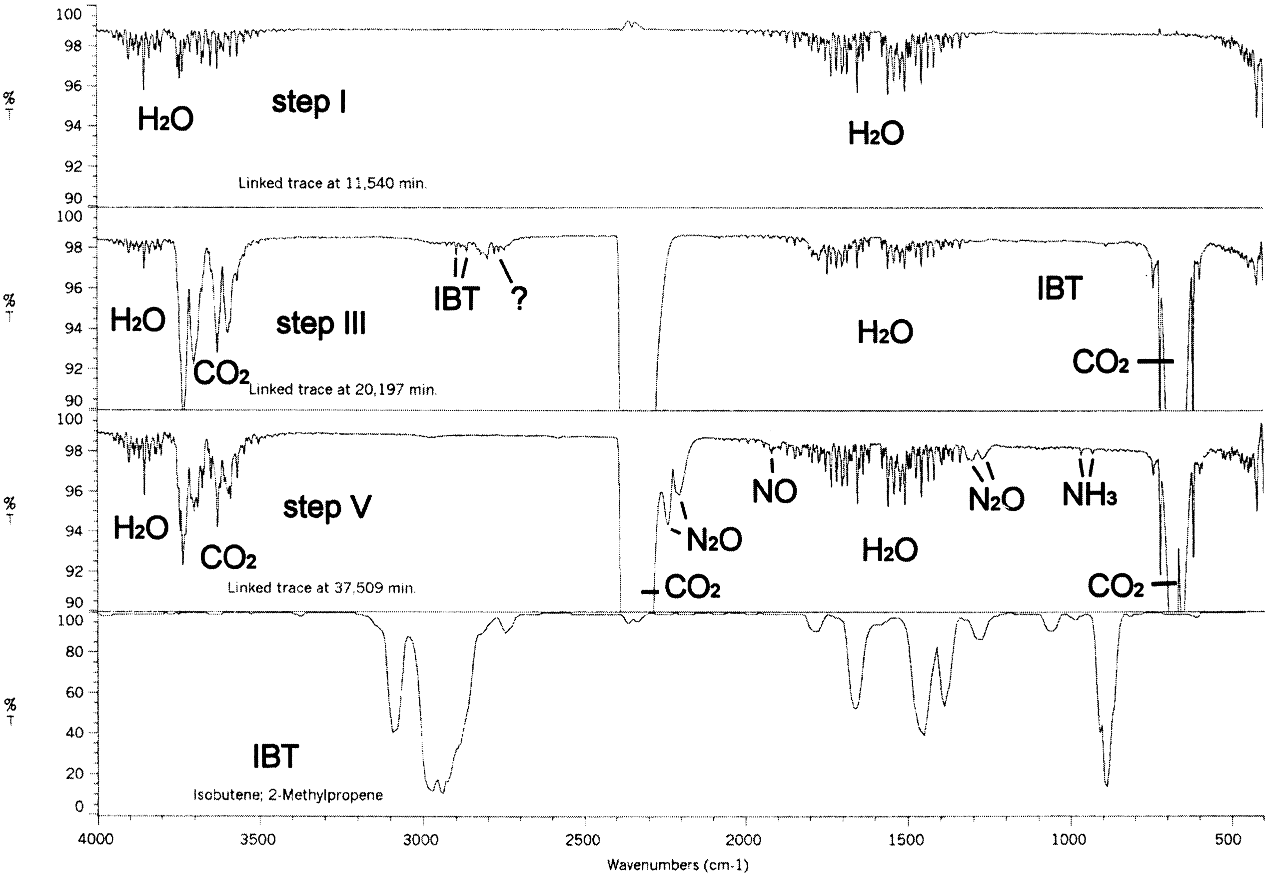


Fig. 6. Selected FT-IR spectra for identification of evolved gasses during the decomposition and pyrolysis of compound **4**. The last spectrum is that of isobutene or 2-methylpropene, for comparison.

of H_2TEBIDA acid and [Cu(TEBIDA)(H_2O)$_2$] giving supramolecular 2D layered framework which connect to each other by non-bonding interactions between these bulky aliphatic groups (oriented towards the external faces of such layers). Compound **3** and **4** agree well with all structural co-relations previously stated for mixed-ligand copper(II) complexes with equimolar Cu(II)/IDA or IDA-like/*N*(heterocyclic donor). Interestingly, TEBIDA ligand exhibits an unexpected *fac*-O_2+N(apical) conformation in compound **5**, explained on the basis of its convenience to develop a molecular recognition process which should better enable a π,π-stacking interaction (involving the two pyridyl rings of both 2,2′-bipy ligands) to form 'pairs of complex molecules'.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 190577 for H_2TEBIDA acid (compound **1**), CCDC No. 190578 for [Cu(TEBIDA)(H_2O)$_2$] (compound **2**), CCDC No. 190579 for $\{[Cu(TEBIDA)(Him)]\cdot 2H_2O\}_n$ (compound **3**), CCDC No. 190580 for $\{[Cu(TEBIDA)(5MeHim)]\cdot H_2O\}_n$ (compound **4**) and CCDC No. 190581 for [Cu(TEBIDA)(2,2′-bipy)(H_2O)]$\cdot 4.5H_2O$ (compound **5**). 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; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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