

Hydrothermal Synthesis, Crystal Structures and Effect of Non Bonding Interactions in Crystal Packing of Two Mixed-Ligand Metal Complexes with Glycolato and 2,2'-Dipyridylamine and with Benzilato and Imidazole

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Abstract. Two new mixed-ligand complexes [Fe(HG)₂(dipyam)] (**1**) (HG = glycolato and dipyam = 2,2'-dipyridylamine) and [Cu(HB)₂(im)₂·2H₂O] (**2**) (HB = benzilato and im = imidazole) have been hydrothermally synthesized and structurally characterized by X-ray diffraction. In both cases the metallic centre is in an octahedral environment, strongly distorted in **2** (4+2 coordination). The α -hydroxycarboxylato ligands (glycolato or benzilato) present different coordinative behaviour, bidentate chelate through the hydroxyl oxygen and one carboxy oxygen in **1** and through the

two oxygen atoms of the carboxylate group in **2**. The complexes are extended into 2D frameworks through hydrogen bonding and $\pi\cdots\pi$ or C-H $\cdots\pi$ interactions. The complexes were also characterized by elemental analysis, FT-IR and UV-vis spectroscopy and room temperature magnetic measurements.

Keywords: Hydrothermal synthesis; Copper; Iron; Mixed-ligand complexes; Supramolecular chemistry; Crystal structures

Introduction

Extended frameworks of coordination compounds based on non-covalent intermolecular interactions like hydrogen bonds [1, 2], $\pi\cdots\pi$ [3] and/or C-H $\cdots\pi$ interactions [3, 4], are currently of great interest because of their intriguing topologies and their potential applications. α -hydroxycarboxylato ligands may exhibit various coordination modes and provide potential intermolecular interactions such as hydrogen bonds involving the hydroxyl and carboxylate functionalities, and $\pi\cdots\pi$ and C-H $\cdots\pi$ interactions when present aromatic substituents. The possibilities of formation of supramolecular arrays can be also promoted by the use of auxiliary ligands such as: imidazole and 2,2'-dipyridylamine, with N-H groups potentially donors in hydrogen bonds and with aromatic rings suitable to establish $\pi\cdots\pi$ and/or C-H $\cdots\pi$ interactions. In this paper, we report the preparation, properties and a detailed structural analysis of two new mixed-ligand complexes with iron(II) and copper(II).

Results and Discussion

Crystalline compounds [Fe(HG)₂(dipyam)] (**1**) and [Cu(HB)₂(im)₂·2H₂O] (**2**) were synthesized in water at pH \approx

7 by hydrothermal reaction. Compound **1** has been obtained by reaction of iron(II) chloride, glycolic acid, 2,2'-dipyridylamine and sodium carbonate in 1:2:1:1 ratio, and compound **2** by reaction of copper(II) hydroxide-carbonate, benzoic acid and imidazole in 0.5:2:2 ratio. Both compounds are stable in air and have high melting points. Compound **1** is very poorly soluble in both polar and apolar solvents, however **2** is soluble in methanol and ethanol.

Structural analysis

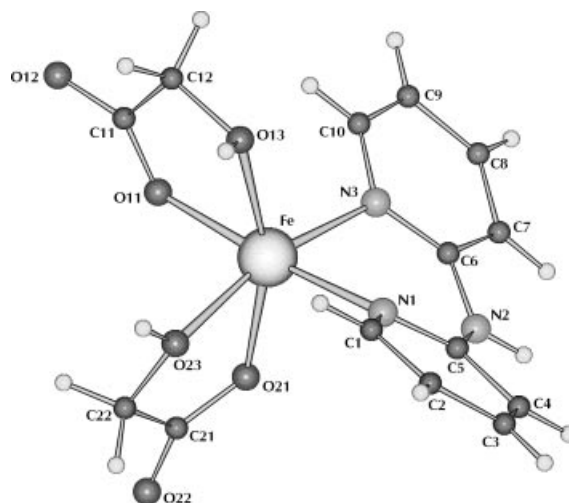
Selected interatomic distances and angles are listed in Table 1, and the main hydrogen bonds in Table 2. Figures 1 and 2 show drawings of structures of compounds **1** and **2**, respectively, together with the atom-numbering schemes used.

The structure of **1** is based on neutral units [Fe(HG)₂(dipyam)], where two monoanionic O,O'-bidentate glycolato ligands (HG⁻) chelate the iron(II) ion through one carboxy and the hydroxyl oxygen atoms to form two five-membered chelate rings (Figure 1). The octahedral coordination around each iron(II) ion is completed by two nitrogen atoms of one 2,2'-dipyridylamine ligand that forms a six-membered chelate ring with a boat conformation. The main deviations from the ideal coordination polyhedron are the chelating angles O_{hydroxyl}-Fe-O_{carboxy} [74.57 and 76.95°] and N-Fe-N [81.76°]. The configuration around the iron(II) ion can be described with the configuration index [OC-6-32] [5], whereas in similar glycolato complexes the configuration around the metal atom is different, for instance, [Cu(HG)₂(2,2'-bipy)] [6] where the hydroxyl groups of the

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Table 1 Selected interatomic bond distances/Å and angles/° for **1** and **2**.

	1		2
Fe-O11	2.0949(15)	Cu-O11	2.002(3)
Fe-O13	2.1352(15)	Cu-O12	2.547(3)
Fe-O21	2.1423(14)	Cu-O21	2.006(3)
Fe-O23	2.1378(16)	Cu-O22	2.563(3)
Fe-N1	2.1466(17)	Cu-N1	1.952(4)
Fe-N3	2.1425(17)	Cu-N3	1.951(4)
O11-Fe-O13	76.95(6)	N3-Cu-N1	178.15(19)
O13-Fe-O23	92.78(6)	N1-Cu-O11	90.09(19)
O13-Fe-O21	160.83(6)	N1-Cu-O21	88.89(13)
O11-Fe-N3	96.80(6)	N3-Cu-O12	92.57(15)
O23-Fe-N3	165.94(6)	O11-Cu-O12	56.17(11)
O11-Fe-N1	175.06(6)	N3-Cu-O22	93.75(14)
O23-Fe-N1	90.37(6)	O11-Cu-O22	121.66(11)
N1-Fe-N3	81.76(6)	O12-Cu-O22	173.38(11)
O11-Fe-O23	91.96(6)	N3-Cu-O11	91.13(14)
O11-Fe-O21	88.94(6)	N3-Cu-O21	89.84(16)
O23-Fe-O21	74.57(6)	O11-Cu-O21	177.61(14)
O13-Fe-N3	99.87(6)	N1-Cu-O12	89.27(14)
O21-Fe-N3	94.56(6)	O21-Cu-O12	125.96(11)
O13-Fe-N1	98.60(6)	N1-Cu-O22	84.42(14)
O21-Fe-N1	95.88(6)	O21-Cu-O22	56.08(11)

**Figure 1** Molecular structure of [Fe(HG)₂(dipyam)] (**1**).

glycolato ligand are *trans*, [OC-6-33], and [Ni(HG)₂(py)₂·2H₂O] [7] where the carboxylate groups are *trans* [OC-6-13]. Note that, when the α -hydroxycarboxylato ligand acts as O,O'-bidentate the chelate metal-O_{carboxylate} distances are usually shorter than the metal-O_{hydroxyl} distances, however in **1**, one of the glycolato ligands shows similar metal-O_{carboxylate} and metal-O_{hydroxyl} distances [Fe-O21 = 2.1423 and Fe-O23 = 2.1378 Å]. The Fe-N bond distances are similar to those found in ¹/₂[Fe(oxa)(dipyam)] (oxa = oxalato) [8].

In compound **2** the asymmetric unit is composed of the neutral complex [Cu(HB)₂(im)₂], where HB is a monoanionic O,O'-bidentate benzilato ligand, and two crystal water molecules (Figure 2). The coordinated carboxylate groups of the benzilato ligands form four-membered unsymmetrical chelate rings. The copper(II) ion adopts a distorted octahedral coordination (4+2) similar to the mixed-ligand complexes with imidazole and carboxylate

derivates ligands [9–13]. The four closest donor atoms are two nitrogen atoms of imidazole ligands and two oxygen atoms of the carboxylate groups forming a distorted square-planar arrangement. Two longer out-of-plane Cu-O bonds from the remaining oxygen atoms of the carboxylate groups complete the strongly distorted octahedral coordination of the copper(II) ion. The configuration around the copper(II) ion is [OC-6-11]. The Cu-N bond lengths agree to those reported in other copper(II) complexes with imidazole [9, 13–15]. The Cu-O distances are in close agreement to those found similar copper(II) complexes with a 4+2 coordination type [9–13]. The longest Cu-O bond lengths [2.547 and 2.563 Å] are shorter than the sum of the van der Waals radii of oxygen and copper {*r*_{vdw}(Cu) = 1.40 Å and *r*_{vdw}(O) = 1.50 Å [16]}.

In both compounds, the nature of the α -hydroxycarboxylato (glycolato and benzilato), imidazole and 2,2'-dipyridylamine ligands allows the formation of supramolecular architectures based on hydrogen bonding (Table 2) and $\pi\cdots\pi$ or C-H $\cdots\pi$ interactions.

Table 2 Main intermolecular hydrogen bond distance/Å and angles/°.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Compound 1				
N2-H20 \cdots O12 ⁱ	0.846(15)	2.060(16)	2.902(2)	174(2)
O23-H23 \cdots O22 ⁱⁱ	0.867(17)	1.752(17)	2.610(2)	171(3)
O13-H13 \cdots O21 ⁱⁱⁱ	0.868(16)	1.789(17)	2.657(2)	179(3)
i: x, -y, z-1/2; ii: x, y+1, z;				
Compound 2				
O13-H13 \cdots O12	0.82	2.13	2.611(4)	117.6
O13-H13 \cdots O22 ⁱ	0.82	2.19	2.917(4)	147.6
O23-H23 \cdots O22	0.82	2.09	2.601(4)	119.9
O23-H23 \cdots O12 ⁱⁱ	0.82	2.09	2.810(4)	146.6
N2-H20 \cdots O1w	0.89(2)	1.90(2)	2.773(6)	170(5)
N4-H40 \cdots O2w ⁱⁱⁱ	0.76(4)	2.00(4)	2.747(6)	170(5)
O1w-H12 \cdots O11 ^{iv}	0.67(4)	2.22(4)	2.844(6)	156(5)
O1w-H11 \cdots O13 ^v	0.91(6)	1.94(6)	2.848(6)	174(6)
O2w-H21 \cdots O21	0.88(2)	1.95(3)	2.809(5)	165(7)
O2w-H22 \cdots O23 ⁱ	0.97(5)	1.76(5)	2.720(5)	170(4)
i: x+1,y,z; ii: x-1, y, z; iii: x, y, z+1; iv: x, y, z-1; v: x-1, y, z-1				

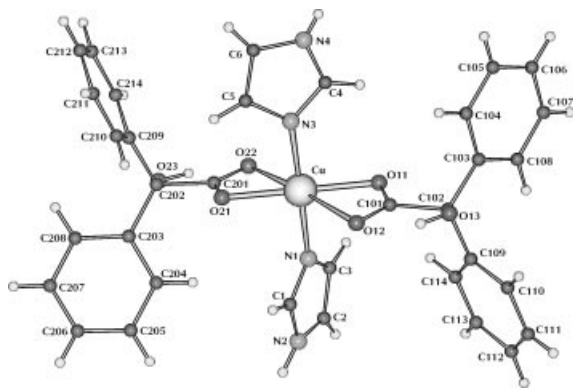


Figure 2 Molecular structure of $[\text{Cu}(\text{HB})_2(\text{im})_2] \cdot 2\text{H}_2\text{O}$ (**2**). Water molecules omitted for clarity.

In **1**, the shortest hydrogen bonds, between the hydroxyl groups of the glycolato ligands and the oxygen atoms (coordinated and non-coordinated) of one carboxylate group of adjacent molecules, form a polymeric chain along the crystallographic b axis. These chains are linked by additional hydrogen bonds involving the NH groups of the 2,2'-dipyridylamine ligands as donors and non-coordinated carboxylate oxygen atoms as acceptors, resulting in an infinite two-dimensional network in the crystallographic bc plane (Figure 3). On the other hand, $\pi \cdots \pi$ interactions are also observed between one pyridine ring [Cg(1): N3-C6-C7-C8-C9-C10] of the 2,2'-dipyridylamine ligand and an analogous ring of a neighbouring molecule $\{d[\text{Cg}(1) \cdots \text{Cg}(1)^i]: 3.8 \text{ \AA}$, symmetry code $i: -x, -y, -z$, dihedral angle $\alpha: 0.02^\circ\}$. These $\pi \cdots \pi$ interactions join two sheets resulting a new two-dimensional supramolecular organization (Figure 4).

In **2**, the intramolecular hydrogen bonds involving the hydroxyl group and the non-coordinated carboxy oxygen atoms of the same benzilato ligand are the strongest. In this case, the supramolecular organization is a consequence of the existence of intermolecular hydrogen bonds and C-H \cdots π interactions. Each benzilato ligand establishes different

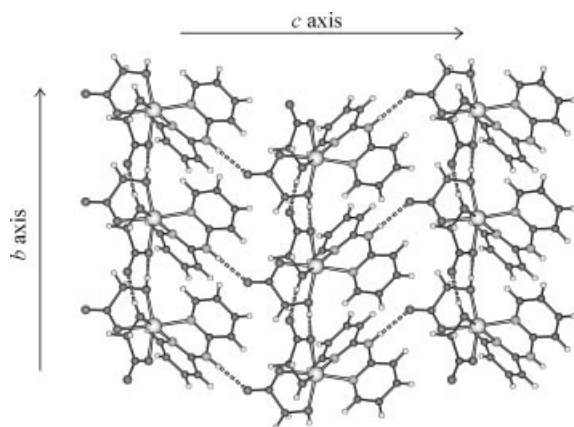


Figure 3 View of the 2D structure generated by hydrogen bonds in **1**.

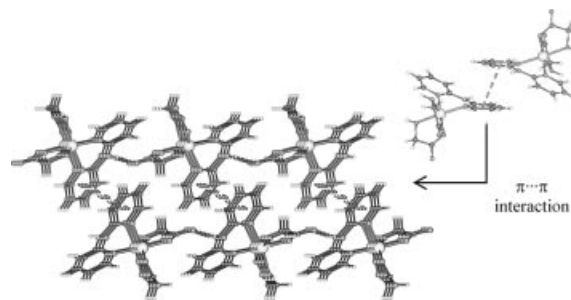


Figure 4 View of the two-dimensional structure generated by $\pi \cdots \pi$ interactions in **1**.

edge-to-face C-H \cdots π interactions, one of them promotes the formation of intramolecular interactions between one C-H group of the benzilato as donor and one imidazole ligand as acceptor [C204-H204 \cdots Cg(1), Cg(1): N1-C1-N2-C2-C3, $d(\text{H} \cdots \text{Cg}): 3.01 \text{ \AA}$, $d(\text{C} \cdots \text{Cg}): 3.92 \text{ \AA}$], and the other benzilato ligand generates intermolecular C-H \cdots π interactions between one C-H group as donor and one phenyl ring of neighbouring analogous benzilato ligand as acceptor [C106-H106 \cdots Cg(2)ⁱ, Cg(2): C109-C110-C111-C112-C113-C114, symmetry code $i: x, y, z+1$, $d(\text{H} \cdots \text{Cg}): 2.97 \text{ \AA}$, $d(\text{C} \cdots \text{Cg}): 3.77 \text{ \AA}$] creating a polymeric chain along the crystallographic c axis (Figure 5). Compound **2** adopts a non-centrosymmetric packing (chiral space group $P2_1$) and the different C-H \cdots π interactions involving the ligands could be responsible of this spontaneous resolution as has been also observed in other compounds [17]. Several hydrogen bonds involving the water molecule as donor and as acceptor (Figure 5 and Table 2) stabilize the chains generated by C-H \cdots π interactions. Also other hydrogen bonds involving the hydroxyl group as donor and as acceptor, and carboxy oxygen atoms as acceptor and the water molecule as donor (Table 2), respectively, join the chains forming a two-dimensional network in the crystallographic ac plane (Figure 6).

Infrared spectroscopy

The infrared spectra of **1** and **2** show sharp bands in the 3000-3200 cm^{-1} region, which are assigned to the NH

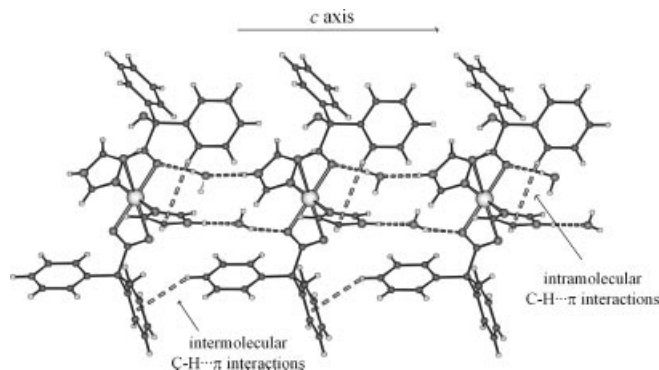


Figure 5 View of the 1D network obtained by C-H \cdots π interactions and hydrogen bonds of **2**.

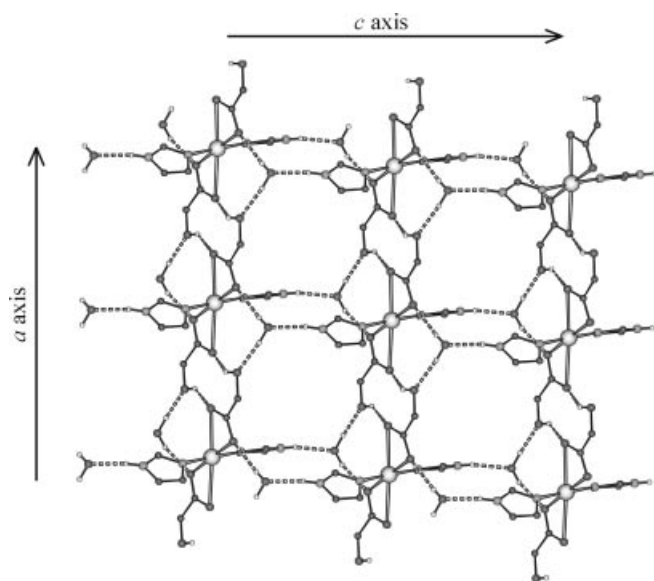


Figure 6 View of the 2D architecture generated by hydrogen bonds in **2**. (Some hydrogen atoms and phenyl groups have been omitted for clarity).

stretching frequency. Compound **1** shows a broad band at 3437 cm^{-1} and compound **2** at 3477 and 3356 cm^{-1} , which correspond to $\nu(\text{OH})$ of the hydroxyl groups of the ligands and the crystallisation water molecule in **2** [18]. The intense bands appearing around 1600 cm^{-1} , which overlap with bands associated with the aminoaromatic ligands, are assigned to the asymmetric COO^- vibration. The bands found at 1368 cm^{-1} for **1** and 1392 cm^{-1} for **2** are assigned to the symmetric COO^- vibration. The value of $\Delta = [\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)]$, 235 cm^{-1} for **1** is typical of monodentate carboxylate groups [19] but the value for **2**, 208 cm^{-1} , is too high for a bidentate-chelate coordination of the carboxylate group, in agreement with the strong unsymmetrical chelate behaviour observed by X-ray studies [19]. In both compounds the band observed in the $420\text{--}450\text{ cm}^{-1}$ region is attributed to $\nu(\text{MO})$ [20].

Electronic and magnetic properties

The electronic spectra of **1** and **2** in the range $250\text{--}1500\text{ nm}$ were recorded in the solid state by diffuse reflectance. The spectrum of **1** consists of two broad bands at 825 and 1060 nm . The observed absorption features are in consonance with those predicted and reported in the literature for a Fe^{II} high spin d^6 octahedral species with a *cis* disposition of the ligands [21]. The electronic spectrum of **2** shows an asymmetric broad band attributable to *d-d* transitions at 630 nm , as expected for octahedral Cu^{II} complexes with a tetragonal distortion [21].

The magnetic effective moments at room temperature, 5.6 B.M. in **1** is close to the value typical of high-spin Fe^{II} centres [22] and 1.9 B.M. in **2** is typical of Cu^{II} species with no $\text{Cu}\cdots\text{Cu}$ interactions [23, 24].

Experimental Section

All reagents and solvents were obtained commercially, glycolic acid (H_2G), 2,2'-dipyridylamine (dipyam) and imidazole (im) from Aldrich, benzoic acid (H_2B) from Avocado, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ and Na_2CO_3 from Fluka and $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2\cdot 0.5\text{H}_2\text{O}$ from Riedel-deHaën. All were used as supplied.

Microanalyses (C, H, N) were carried out with a Fisons EA-1108 elemental analyser. Melting points (m. p.) were carried out with a Gallenkamp MBF-595 apparatus. FT-IR spectra were recorded from KBr pellets ($4000\text{--}400\text{ cm}^{-1}$) or polyethylene-sandwiched Nujol mulls ($500\text{--}100\text{ cm}^{-1}$) on a Bruker Vector 22 and on a Bruker IFS66v spectrometers, respectively. A Shimadzu UV-3101PC spectrophotometer was used to obtain the electronic spectra in the region $250\text{--}1500\text{ nm}$. Magnetic susceptibility measurements were performed at $25\text{ }^\circ\text{C}$ using Johnson Matthey Alfa MSB-MK1 Gouy balance.

Synthesis of the complexes

$[\text{Fe}(\text{HG})_2(\text{dipyam})]$ (**1**)

Under a positive pressure of argon $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (1.0 mmol) was dispersed in 10 mL of degassed water in a Schlenk flask to give a yellowish-green solution. To this solution were added with continuous stirring glycolic acid (H_2G , 2.0 mmol), Na_2CO_3 (1 mmol) and 2,2'-dipyridylamine (dipyam, 1 mmol). The mixture was transferred to a Teflon-lined stainless-steel autoclave and heated at $130\text{ }^\circ\text{C}$ for 5 hours followed by slow cooling at a rate of $3\text{ }^\circ\text{C}\cdot\text{h}^{-1}$. Green crystals of **1** were collected by filtration, washed with water and dried in air.

Data for **1**: Yield: 30% ; m.p. $>250\text{ }^\circ\text{C}$; Anal. Found: C 44.5 , H 4.0 , N 11.0 . Calc. for $\text{C}_{14}\text{H}_{15}\text{FeN}_3\text{O}_6$ (377.14): C 44.6 , H 4.0 , N 11.1% .

IR (ν , cm^{-1}): 3437s , 3167m , 3083m , 3023m , 1635vs , 1603s , 1476s , 1432m , 1368s , 1046m , 1010m , 773m , 557m , 280m . UV-vis (λ , nm): 825 , 1060 . μ_{eff} at $25\text{ }^\circ\text{C}$: 5.6 B.M.

$[\text{Cu}(\text{HB})_2(\text{im})_2]$ (**2**)

$\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2\cdot 0.5\text{H}_2\text{O}$ (0.5 mmol), benzoic acid (H_2B , 2.0 mmol) and imidazole (im, 2.0 mmol) were dispersed in 10 mL of water in a flask with continuous stirring to give a green suspension. The mixture was transferred to a Teflon-lined stainless-steel autoclave and heated at $140\text{ }^\circ\text{C}$ for 10 hours followed by slow cooling at a rate of $1.5\text{ }^\circ\text{C}\cdot\text{h}^{-1}$. Blue crystals of **2** were collected by filtration, washed with water and dried in air.

Data for **2**: Yield: 36% ; m.p. $200\text{ }^\circ\text{C}$; Anal. Found: C 59.5 , H 5.2 , N 8.1 . Calc. for $\text{C}_{34}\text{H}_{34}\text{CuN}_4\text{O}_8$ (690.19): C 59.2 , H 5.0 , N 8.1% .

IR (ν , cm^{-1}): 3478m , 3356s , 3144m , 1613vs , 1600sh , 1550m , 1513m , 1489m , 1448m , 1392m , 1325s , 1169m , 1102m , 750s , 702s , 423w , 275m . UV-vis (λ , nm): 630 . μ_{eff} at $25\text{ }^\circ\text{C}$: 1.9 B.M.

X-ray Crystallography

Crystallographic data were collected on a Bruker Smart CCD diffractometer at 243 K (**1**) and at 293 K (**2**) using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$), and were corrected for Lorentz and polarisation effects. The frames were integrated with the Bruker SAINT [25] software package and the data were corrected for absorption using the program SADABS [26]. The structures were solved by direct methods using the program SHELXS97

Table 3 Crystal and structure refinement data.

Compound	1	2
Empirical formula	C ₁₄ H ₁₅ FeN ₃ O ₆	C ₃₄ H ₃₄ CuN ₄ O ₈
Formula weight	377.14	690.19
Crystal system	monoclinic	monoclinic
Space group	P2/c	P2 ₁
Unit cell dimensions /Å, °		
a	15.210(3)	7.8245(16)
b	5.8118(12)	23.520(5)
c	17.563(4)	9.0209(18)
β	106.656(4)	94.68(3)
Crystal size /mm ³	0.29 x 0.10 x 0.04	0.23 x 0.17 x 0.10
θ Range /°	1.4–30.0	1.7–28.1
Index ranges	–14/21, –8/7, –23/22	–10/8, –31/31, –11/9
Reflections collected	9412	10231
Independent reflections	4000 [R(int)= 0.0317]	7036, [R(int)= 0.0396]
Max/min transmission	1.000/0.842	1.000/0.878
Data/parameters	4000/ 229	7036/451
Goodness-of-fit on F ²	1.005	0.995
Final R indices [I>2σ(I)]	R ₁ = 0.0378 wR ₂ = 0.0744	R ₁ = 0.0619 wR ₂ = 0.0935

[27]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F² using the program SHELXL97 [28]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters, except for the hydrogen atoms of hydroxyl groups, NH groups and water molecules, which were located from a Fourier-difference map and refined isotropically (in some cases the distances O–H and N–H were restrained with DFIX 0.9). For **2**, which crystallized in the chiral space group P2₁, the analysis established unambiguously the absolute structure {Flack's Parameter [29] 0.000(14)}. Drawings were produced with SCHAKAL99 [30]. Special computations for the crystal structure discussions were carried out with PLATON [31]. Crystal data and structure refinement parameters are summarised in Table 3.

Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 252927 and 252928 for compounds **1** and **2**, 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; e-mail: or www:

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