Syntheses and crystal structures of copper complexes of the imidazole ligand

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Two copper(II) complexes, $[Cu(im)_6]Cl_2·4H_2O$ (**1**), and $[Cu(im)_6]Cl_2·2H_2O$ (**2**) (im = imidazole), have been synthesised. In compound **1**, $[Cu(im)_6]^{2+}$ cations and Cl^- counter anions alternately array in an ABAB fashion *via* N–H…Cl hydrogen bonding. There are two kinds of hydrogen bonds, inter- and intramolecular hydrogen bonding interactions, which form 2-D sheets. However, an interesting polymeric network is formed from the weak intermolecular interactions in compound **2**.

Keywords: copper complexes, imidazole, hydrogen bond

The study of imidazole as a complexing agent has been a matter of active interest for many years, mainly because imidazole is involved in important biological processes.[1–3] There are two nitrogen atoms per imidazole molecule. The deprotonated nitrogen atom is able to coordinate to metal ions and a series of compounds based on imidazole and different metal ions has been reported.[4–8] On the other hand, the protonated nitrogen atom in the imidazole molecule is a good hydrogen bonding donor and multi-dimensional supramolecular assemblies can be obtained *via* hydrogen bonding interactions.[9–14] Several structural studies of such complexes have already been published.[15-17] To get more information about molecular architecture and network construction by solvent, the present paper describes the synthesis and structure of copper complexes with the imidazole ligand.

Reaction of $CuCl_2·2H_2O$ with imidazole afforded blue crystals of the title complex (Scheme 1). In the IR spectrum of compound **1**, the peaks at 749, 848, 1072, 1325, and 1534 cm^{-1} are attributed to imidazole. These characteristic peaks shift to 749, 839, 1067, 1386, 1537 cm^{-1} in **2** due to the influence of water molecules in the two complexes. The peaks at 3207 and 3212 cm^{-1} of **1** and **2** respectively are attributed to $\nu_{O–H}$ of the water molecules.

Complex **1** crystallises as blue irregular crystals in P-1 symmetry with the copper(II) ion located on an inversion centre. The complex consists of a hexakis(imidazole)copper(II) cation, two non-coordinated Cl^- anions and four water molecules (Fig. 1). In the $[Cu(im)_6]^{2+}$ cation, the copper ion is coordinated by six imidazoles, exhibiting a trivially elongated octahedron. The four short Cu–N distances in the equatorial plane [Cu–N(1) = 2.127(3) Å and Cu–N(5) = 2.135(3) Å], are comparable to inner sphere Cu–N distances found in other imidazole copper(II) carboxylate complexes.[18-21] The other two imidazole ligands ions, [Cu–N(3) = 2.144(3) Å], lie on the axial positions which deviate only trivially from equivalence. The CuN_4 is co-planar, but the imidazole ligands are oriented in two sets: perpendicular and parallel.

In compound **1**, Cl^- and H_2O exhibit planar geometry, each $[Cu(im)_6]^{2+}$ cation arrays orderly in the middle of the crystal cell and links Cl^- in the ab cell plane via N–H/Cl hydrogen bonding (Fig. 2). The $[Cu(im)_6]^{2+}$ cations and Cl^- counter anions alternatively array in the solid state and crystal plane in an ABAB fashion. Water molecules (their oxygen atoms are in the ab plane) connect each other or link Cl^- via O–H/O or O–H/Cl hydrogen bonding interactions (Table 1).

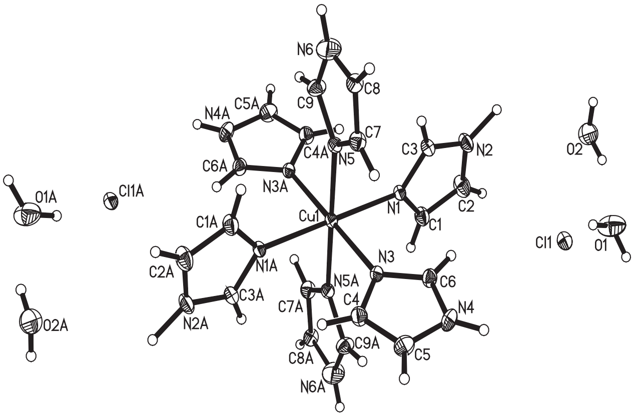
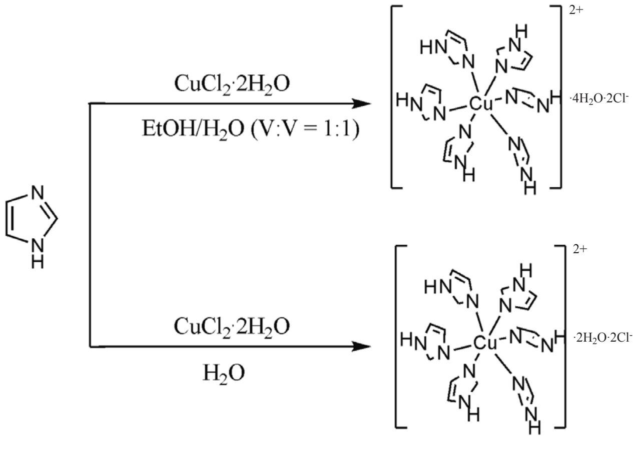


Fig. 1 A view of (**1**) with 30% probability ellipsoid.



Scheme 1

Complex **2**, $[Cu(im)_6]Cl_2·2H_2O$, crystallises in the monoclinic crystal system, and again it is formed of discrete $[Cu(im)_6]^{2+}$ cation and Cl^- anions as shown in Fig.3. The Cu atom is in an octahedral environment formed by N atoms of the imidazole moieties. The bond distances involved in this octahedral geometry, (Cu–N1, Cu–N2 and Cu–N3) are the most close to regular octahedral, ranging from 2.122(12) to 2.161(12) Å. The equatorial ligands are involved in a complex hydrogen bond network that involves the chloride anions and uncoordinated water molecules.

An interesting aspect of this crystal structure is the hydrogen-bonding pattern. The Cl^- ion does not coordinate to the metal atom, but forms hydrogen bonds with the $[Cu(im)_6]^{2+}$ ions and water molecules, Fig.4. There are no unusual features in either the bond lengths or the bond angles in the anion.

The complexes **1** and **2** form three-dimensional networks through intermolecular hydrogen bonds with the counter anions and water molecules. Details of the complex hydrogen-

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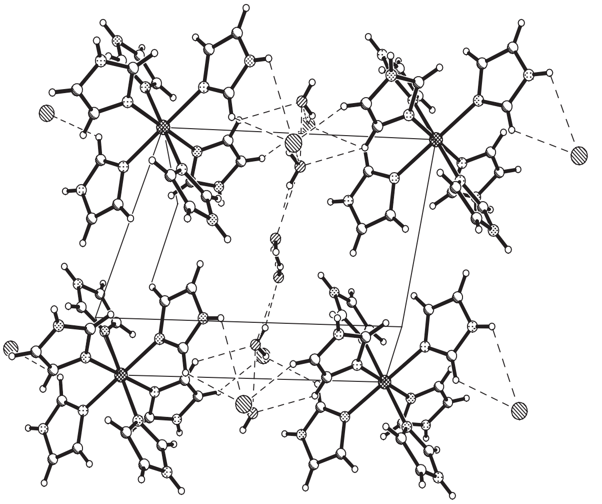

Fig. 2 Unit cell packing of (**1**) showing hydrogen-bonding interactions. Selected bond lengths and angles: Cu(1)–N(1) 2.127(3); Cu(1)–N(5) 2.136(3); Cu(1)–N(3)#1 2.144(3); N(1)–C(1) 1.376(6); N(2)–C(3) 1.332(6); N(1)–Cu(1)–N(1)#1 180.0(2); N(1)–Cu(1)–N(5)#1 90.19(13); N(1)–Cu(1)–N(5) 89.81(13) ;N(5)#1–Cu(1)–N(3)#1 90.52(12). Symmetry transformations used to generate equivalent atoms: #1 –x+2,–y+2,–z.

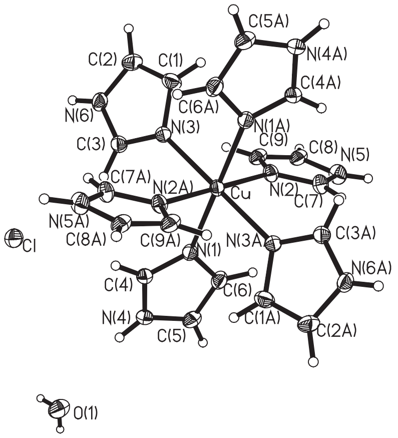

Fig. 3 A view of (**2**) with 30% probability ellipsoid.

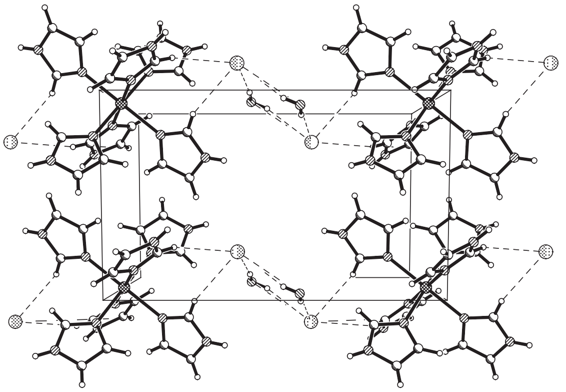

Fig. 4 Unit cell packing of (**2**) showing hydrogen-bonding interactions. Selected bond lengths and angles: Cu–N(2)#1 2.1355(13); Cu–N(1) 2.1221(12); Cu–N(3) 2.1605(12); N(1)–C(4) 1.3143(19); N(1)–C(6) 1.381(2); N(5)–C(7) 1.3549(19). N(1)–Cu(1)–N(1)#1 180.0; N(1)#1–Cu–N(2)#1 87.66(5); N(1)#1–Cu–N(2) 92.34(5); N(1)#1–Cu–N(3)#1 92.84(5); N(2)#1–Cu–N(3)#1 88.56(5). Symmetry transformations used to generate equivalent atoms: #2 x,y,1+z

Table 1 Hydrogen-bonding geometry and close contacts (Å,°) for **1** and **2**

D-H...A	d (D–H)	d(H...A)	d(D...A)	*d*(D-H...A)
Complex **1**[a]				
N(4)–H(4B)...Cl(1)#2	0.86	2.52	3.342(4)	160.6
N(2)–H(2B)...Cl(1)#3	0.86	2.39	3.238(4)	170.0
O(2)–H(2F)...Cl(1)#3	0.86	2.55	3.203(4)	134.2
O(1)–H(1F)...O(1)#4	0.88	1.85	2.712(8)	168.0
O(2)–H(2G)...O(1)	0.83	1.96	2.743(6)	159.3
O(1)–H(1E)...Cl(1)	0.87	2.33	3.171(4)	160.4
Complex **2**[b]				
O(1)–H(1W).. Cl #1	0.79	2.41	3.196(2)	172
O(1)–H(2W).. Cl #2	0.76	2.47	3.209(2)	166
C(4)–H(4)....Cl #3	0.93	2.73	3.4816(16)	139
C(5)– –H(5)... Cl	0.93	2.75	3.6277(19)	157

Symmetry transformations used to generate equivalent atoms:
[a]#1 −*x* + 2,−*y* + 2,−*z* #2 −*x* + 1,−*y* + 2,−*z* + 1 #3 −*x* + 2,−*y* + 1,−*z* + 1 #4 −*x* + 1,−*y* + 1,−*z* + 1.
[b] #1 1/2−*x*,1/2 + *y*,1/2−*z* #2 *x*,*y*,1 + *z* #3 1−*x*,−*y*,1−*z*.

bonding scheme can be created from the deposited cif-files. All the imidazole rings are individually planar. The largest deviations from the mean plane are –0.0027Å at the C6 atom for **1** and 0.0046 Å at the C7 atom for **2**, respectively. Bond lengths and angles within the imidazole rings are in good agreement with the parameters reported for the structure of imidazole itself.[22] In compound **1**, the least-squares plane of the imidazole ligands that contain N1, N2, C1, C2, and C3 makes dihedral angles of 85.0°, 85.6°, 91.2° with the planes defined by N5, N6, C7, C8, C9 and N3, N4, C4, C5, C6, respectively, whereas in **2**, the least-squares plane that contains N1, N4, C4, C5, and C6 makes dihedral angles of 65.9°, 102.5°, 71.6° with the planes defined by N3, N6, C1, C2, C3 and N5, N2, C7, C8, C9, respectively.

The crystals of $[Cu(im)_6]Cl_2·4H_2O$ and $[Cu(im)_6]Cl_2·2H_2O$ (present work) are isomorphous with $[Mn(Im)_6]C1_2·4H_2O$,[23] $[Zn(Im)_6]C1_2·4H_2O$ [24] and $[Ni(Im)_6]C1_2·4H_20$.[25] In these compounds, the $[M(Im)_6]^{2+}$ cations (M = Cu, Mn, Zn, Ni) have octahedral coordination and exhibit a slight tetragonal distortion. The average Cu-N distance of the title compounds is about 2.1357 to 2.1409 Å, which is slightly longer than the normal distance of copper (imidazole) complexes,[26] but the value falls into the normal range of Cu-N.[27] But in the crystal of $[Cu(im)_6][NO_3]$,[28] the bond lengths of equatorial Cu-N(1B) and Cu-N(1C) are 2.049(2)Å, 2.012(2) Å respectively. The axial Cu-N length is 2.593(3) Å, which enormously exceeds the mean of the equatorial distances (2.031 Å**)**, therefore there is far more distortion from a regular octahedron around the Cu atom than is reported for the title compounds.

We have successfully synthesised and characterised two novel supramolecular assemblies. It is worth noting that although the reaction conditions differ only in solvent, the structures of **1** and **2** are completely different: complex **1** belongs to the triclinic system, space group P-1, while compound **2** falls into the monoclinic system, space group P 21/n. In **1**, the $[Cu(im)_6]^{2+}$ cations and Cl^- counter anions alternately array in the solid state and crystal plane in an ABAB fashion. There are two kinds of hydrogen bonds: inter- and intramolecular hydrogen bonding interactions which form 2-D sheets. But only intramolecular hydrogen bonding interactions exist in compound **2**, which is polymeric. From these examples we know that hydrogen bonding will play a more important role in defining the overall supramolecular architecture.

Experimental

FT-IR spectra were recorded on a BIO-RAD FT-165 IR spectrometer using KBr pellets. Elemental analysis was carried out with a Carlo Erba-1106 Instrument. All reagents were used as received.

Synthesis of $[Cu(im)_6]Cl_2{\cdot}4H_2O$ (**1**): Imidazole (0.681 g, 10 mmol) was dissolved in 10 ml EtOH/H_2O (V : V = 1 : 1) solution, and to the resultant solution was added 10 ml of double-distilled water containing $CuCl_2{\cdot}2H_2O$ (0.170 g, 1 mmol). The resulting solution was heated at 373 K for 96 h. After cooling to room temperature, blue crystals were obtained in a yield up to 37.65%. Anal. Calc. for **1**: C, 35.1; H, 5.2; N, 27.3. Found: C, 35.6; H, 5.2, N, 27.4%. *Cell parameters for* **1**: Z = 1, Mr = 615.00, Triclinic system, space group P-1 with a = 8.8097(18) Å, b = 9.0812(18) Å, c = 10.586(2) Å, α = 75.08(3)°, β = 83.14(3)°, γ = 61.84(3)°, R_1 = 0.0562, wR_2 = 0.1607.

Synthesis of $[Cu(im)_6]Cl_2{\cdot}2H_2O$ (**2**): The procedure was similar to that for **1** except that the imidazole was dissolved in 10 ml H_2O solution, (43% yield). Calc. for **2**: C, 37.3; H, 4.8; N, 29.2 Found: C, 37.2; H, 4.75; N, 29.1%. *Cell parameters for* **2**: Z = 2, Mr = 578.97, monoclinic system, space group P 21/n with a = 8.073(2) Å, b = 13.239(2) Å, c = 15.0810(10) Å, β = 97.940(10)°, R_1 = 0.0434, wR_2 = 0.1243.

Suitable single crystals of **1** and **2** were carefully selected with an optical microscope and glued to thin glass fibres. The diffraction data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-*Ka* radiation (λ = 0.71073Å) at 291K. An empirical absorption correction was applied using the SADABS program.[29] The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package.[30] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of imidazole were generated geometrically, no attempts were made to locate the hydrogen atoms of water.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC: (1) 660809; (2) 669533 Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

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