

ORIGINAL PAPER

Copper oxalate complexes: synthesis and structural characterisation[‡]

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Six copper(II) oxalate complexes, namely $\{K_2[Cu(ox)_2]\}_n$ (**1**), $\{(Hiz)_2[Cu(ox)_2]\}_n$ (**2**), $\{[Cu(ox)(N-BzIiz)_2]\}_n$ (**3**), $(HMeiz)_2[Cu(ox)_2]$ (**4**), $\{[Cu(ox)(Meiz)_2]\}_n$ (**5**), and $[Cu(Hox)_2(H_2O)_2](N-BzIiz)$ (**6**) where ox = oxalate ion, iz = imidazole, N-BzIiz = *N*-benzylimidazole, Meiz = 2-methylimidazole, were synthesised and characterised by single crystal X-ray diffraction (complexes **1–5**) or powder X-ray diffraction (compound **6**). The three-dimensional crystal packing structures of **2**, **4**, and **5** are consolidated by intermolecular hydrogen bonds linking the oxygen atom of the oxalate group and the amine or imine group of the imidazole-based part into chains. The molecules of complex **6** are held together by intermolecular hydrogen bonds between the oxygen atoms of the oxalate group and coordinated water molecules.

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Introduction

Many authors have tried to obtain copper complexes of various nuclearities and dimensionalities. In the Cambridge Crystallographic Data Centre it is possible to find a number of oxalate complexes with different imidazole-based ligands. Reference may be made to the following: some studies published in 2011 (Jin & Lin, 2011; Chen et al., 2011; Kaştaş et al., 2011; Xu, 2011) or in 2013 (Zhu & Zhang, 2013; Sánchez et al., 2013). However, there is little information and only a few sources related to oxalate copper complexes with 2-methylimidazole-based ligand. Studies were performed on this group of complexes by Julve et al. (1984) and Geiser et al. (1987). On viewing the Database, it was clearly possible to enrich the last group of oxalate copper complexes in particular, specifically with the *N*-benzylimidazole-based ligand (Meng et al., 2006).

The preparation method and reaction conditions are of crucial importance because oxalate-derived ligands exhibit various coordination modes which lead to manifold molecular structures (mononuclear, dinuclear, or polynuclear) and have received considerable attention (Akhrif et al., 1999; Duan et al., 2008; Leong & Vittal, 2011; Kuchár et al., 2009). The data reported in the literature also support the idea that oxalate and carboxylate ligands create various types of structures even with the same type of ligand (Deacon & Phillips, 1980).

In recent years, several structural–magnetic correlations have been proposed and the influence of the Jahn–Teller distortion effect on oxalate-bridged copper(II) sites was described (Kang, 2005; Murphy & Hathaway, 2003). It is important to note that the Jahn–Teller effect leads to some unusual features in molecular magnetism. In this case, the copper(II) systems have been the most frequently studied (Halcrow, 2013).

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Table 1. Crystallographic data for **1–6** copper(II) complexes

	1	2	3	4	5	6
Chemical formula	(C ₂ CuK ₂ O ₄) _n	(C ₁₀ H ₁₀ CuN ₄ O ₈) _n	(C ₂₂ H ₂₀ CuN ₄ O ₄) _n	C ₁₂ H ₁₄ CuN ₄ O ₈	(C ₁₀ H ₁₂ CuN ₄ O ₄) _n	C ₁₄ H ₁₆ CuN ₂ O ₁₀
FW	229.76	377.76	467.96	405.82	315.79	435.83
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P2 ₁ /c	P-1	P2 ₁ /c	C2/c	Pca2 ₁	P2 ₁ /a
T/K	150(2)	150(2)	150(2)	293(2)	100(1)	293(1)
Cell lengths						
a/Å	4.8800(2)	3.6170(2)	5.6080(2)	15.800(5)	19.4407(5)	10.9164(3)
b/Å	6.6520(3)	9.4000(6)	7.7360(7)	19.062(1)	8.2161(2)	11.1727(3)
c/Å	13.5020(4)	10.023(1)	22.985(1)	14.319(6)	7.8900(2)	10.7713(3)
Cell angles						
α/°	90	106.617(6)	90	90	90	90
β/°	104.499(3)	97.164(6)	103.409(4)	117.09(6)	90	104.836(3)
γ/°	90	94.486(5)	90	90	90	90
Cell volume						
V/Å ³	424.34(3)	321.67(4)	969.99(11)	3839(12)	1260.25(5)	1269.92(7)
Formula units (Z)	2	1	2	8	4	2
λ/Å (Mo/CoK _α)	0.71073	0.71073	0.71073	0.71073	0.71073	1.78892
ρ _{calc} /(g cm ⁻³)	2.487	1.950	1.602	1.404	1.664	1.7039
R factor	0.0183	0.0269	0.0237	0.0423	0.0315	0.0382
[I > 2σ(I)]						
wR factor	0.0439	0.0675	0.0570	0.1185	0.0626	0.0398
GOF	1.052	1.115	1.072	1.098	1.051	1.640

A previous work reported on the synthesis and crystal structure of Cu(II) complexes containing oxalate bridges (Matelková et al., 2013). The present study reports on the synthesis and structural study of six copper(II) compounds. Of the six copper(II) complexes, compounds {(Hiz)₂[Cu(ox)₂]}_n (**2**) and {[Cu(ox)(Meiz)₂]}_n (**5**), where ox = oxalate ion, iz = imidazole, Meiz = 2-methylimidazole, have been previously reported (Chattopadhyay et al., 1995; Geiser et al., 1987).

Experimental

The chemicals were purchased from commercial sources and were used without further purification. K₂[Cu(CN)₃] was prepared by combining a solution of CuCN and KCN in an 1 : 2 molar ratio.

The single-crystal X-ray diffraction measurements for complexes **1–3** were performed on a Bruker-Nonius KappaCCD diffractometer (Nonius BV, Delft, The Netherlands) at 150 K using MoK_α radiation monochromated by graphite. The intensity data were corrected for Lorentz and polarisation factors. The structures were resolved by the direct methods with SHELXS-2013 (Sheldrick, 2008) or SIR-2011 (Burla et al., 2012) and refined by the full-matrix least squares procedure with SHELXL-2013 (Sheldrick, 2015) or CRYSTALS (Betteridge et al., 2003). The multi-scan absorption corrections were made using the SADABS numerical method (Gaussian integration, Bruker (2001)). Geometrical analyses were performed using SHELXL or CRYSTALS.

The single-crystal diffraction data for complexes **4** and **5** were collected on an Oxford Diffraction

Kappa geometry Gemini R diffractometer (Oxford, UK) equipped with a Ruby CCD area detector using graphite monochromated MoK_α radiation at 293(2) K (**4**) or 100(1) K (**5**). The diffraction intensities were integrated and the Lorentz-polarisation and the FACE-absorption correction were performed using CrysAlis CCD RED software (Oxford Diffraction Ltd., 2013). The crystal structures were resolved by direct methods using SHELXS-2013 (Sheldrick, 2008) and refined by the full-matrix least squares procedure with SHELXL-2014 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. All C—H hydrogen atoms were placed in idealised positions and refined as riding atoms with isotropic parameters 1.2 times those of the heavy atoms to which they are attached.

In a final difference Fourier map of complex **4**, a highly disordered electron density, occupying two cavities of ca 410 Å³ per unit cell, was observed. This residual electron density was difficult to model, hence the SQUEEZE routine in PLATON was used to eliminate this contribution of the electron density in the solvent region from the intensity data (Spek, 2015). The solvent-free model was employed for the final refinement. The solvent molecules were not included in the calculation of the overall formula mass, density, and absorption coefficient.

The powder data of **6** were collected using a STOE Stadi-P transmission diffractometer (Darmstadt, Germany), equipped with a Co-tube and with a linear PSD. The powder pattern of **6** was analysed using the multi-purpose program CMPR (Toby, 2005) with auto-indexing program DICVOL06 (Boultif & Lourt, 2004). Le Bail pattern decomposition and Rietveld refinement were performed in the program JANA2006

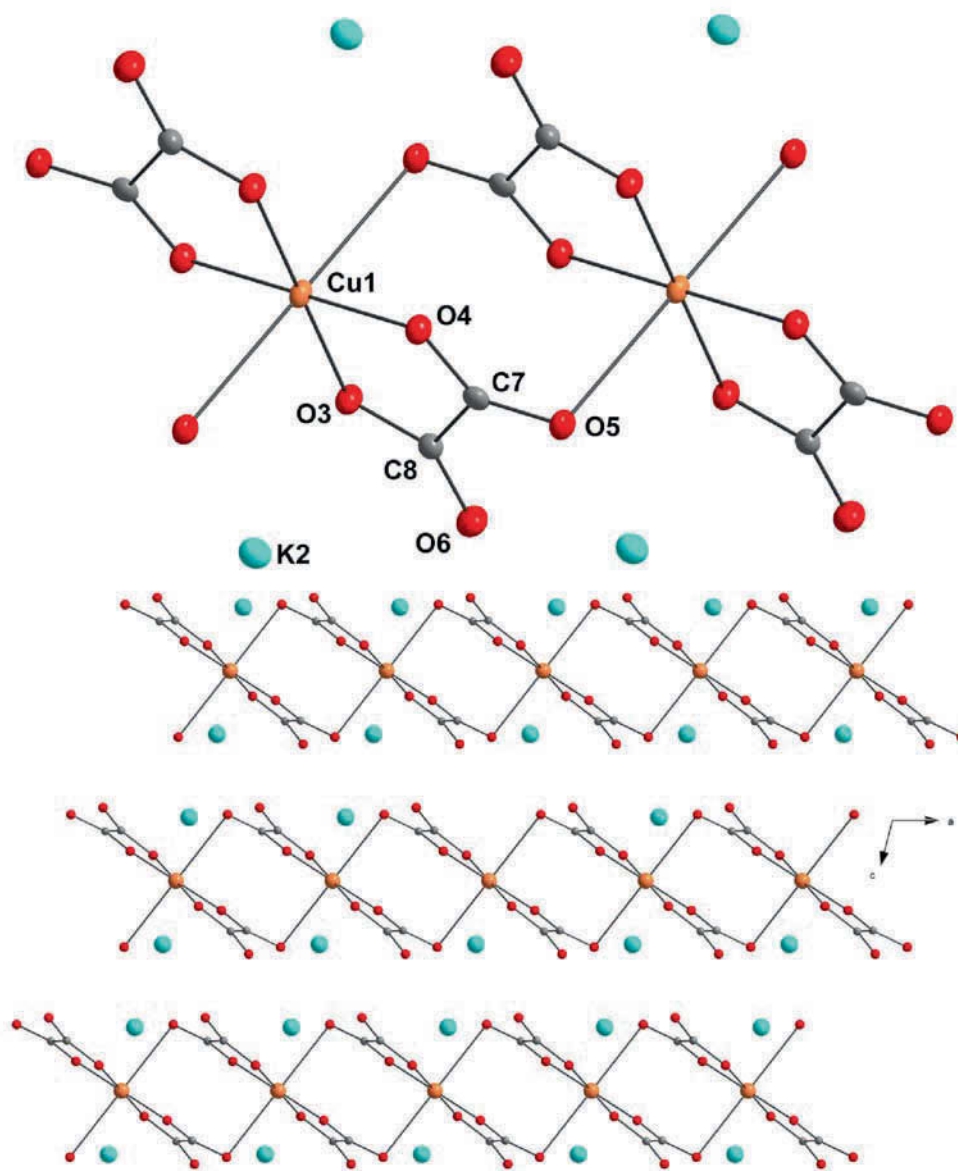


Fig. 1. DIAMOND drawing of $\{K_2[Cu(ox)_2]\}_n$ (**1**) with atom numbering scheme of asymmetric unit. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are removed for clarity. Packing diagram of compound **1** (below). Symmetry operations: (i) x, y, z , (ii) $-x, y + 1/2, -z + 1/2$; (iii) $-x, -y, -z$; (iv) $x, -y + 1/2, z + 1/2$.

(Petříček et al., 2014). The ab-initio structure solution was evaluated using FOX (Favre-Nicolin & Černý, 2002). For the plots of the structures, the DIAMOND program was used (Brandenburg & Putz, 2015).

The infrared spectra of five prepared compounds (**1**, **2**, **3**, **4**, and **6**) were measured on a Magna-FTIR-750 spectrometer (Nicolet, Thermo Fischer Scientific, Waltham, MA, USA) in KBr pellets in the 4000–400 cm^{-1} region.

Initially, an attempt was made to prepare cyanide complexes with manganese central atom, hence in accordance with the literature, the process of diffusion was used. It is common to use an H-tube for this purpose but, in this case, another and original synthetic way was sought, namely preparation

in a test-tube. As stated above, for the preparation of cyanide complexes, a test-tube, a source of manganese ions (MnC_2O_4) and a source of cyanide bridges ($K_2[Cu(CN)_3]$) were needed.

Paradoxically, the test-tube synthesis method represents an efficient procedure for synthesising compounds $\{K_2[Cu(ox)_2]\}_n$ (**1**), $\{(Hiz)_2[Cu(ox)_2]\}_n$ (**2**), and $\{[Cu(ox)(N-BzIiz)_2]\}_n$ (**3**). These complexes were prepared in the same way, by the reaction of an aqueous methanol solution (5 mL + 5 mL) of MnC_2O_4 (0.343 mmol) and 2-methylimidazole (0.341 mmol) (**1**) (imidazole (0.341 mmol) (**2**) or *N*-benzylimidazole (0.341 mmol) (**3**)) with $K_2[Cu(CN)_3]$ (0.114 mmol, also dissolved in an aqueous methanol solution (3 mL + 3 mL)). The solutions were separated into two parts,

Table 2. Selected bond lengths (Å) and angles (°) of **1–6**

$\{\text{K}_2[\text{Cu}(\text{ox})_2]\}_n$ (1)			
Cu1—O3	1.936(1)	O3—Cu1—O4	86.09(6)
Cu1—O4	1.927(1)	O3—Cu1—O3	180.00
Cu1—O5	2.648(1)	O3—Cu1—O5	88.49(5)
$\{(\text{Hiz})_2[\text{Cu}(\text{ox})_2]\}_n$ (2)			
Cu1—O5	1.934(2)	O5—Cu1—O6	85.34(8)
Cu1—O6	1.928(2)	O5—Cu1—O5	180.00(8)
$\{[\text{Cu}(\text{ox})(\text{N-BzIiz})_2]\}_n$ (3)			
Cu1—O1	1.977(1)	O1—Cu1—N1	90.31(5)
Cu1—N1	2.030(1)	O1—Cu1—O2	76.57(4)
Cu1—O2	2.375(1)	O1—Cu1—O1	180.00(5)
$(\text{HMeiz})_2[\text{Cu}(\text{ox})_2]$ (4)			
Cu1—O1	1.912(6)	O1—Cu1—O2	84.4(2)
Cu1—O2	1.943(4)	O1—Cu1—O5	174.3(2)
Cu1—O5	1.956(6)	O1—Cu1—O6	95.5(2)
Cu1—O6	1.924(4)	O5—Cu1—O6	85.0(2)
$\{[\text{Cu}(\text{ox})(\text{Meiz})_2]\}_n$ (5)			
Cu1—N1	1.971(6)	N1—Cu1—N4	95.5(2)
Cu1—N4	1.977(6)	N1—Cu1—O1	92.9(2)
Cu1—O1	1.968(4)	N1—Cu1—O2	156.2(2)
Cu1—O2	1.992(5)	N1—Cu1—O3	115.0(2)
Cu1—O3	2.257(5)	O2—Cu1—O3	88.0(2)
$[\text{Cu}(\text{Hox})_2(\text{H}_2\text{O})_2](\text{N-BzIiz})$ (6)			
Cu1—O2	1.92(1)	O2—Cu1—O3	83.3(5)
Cu1—O3	1.96(1)	O2—Cu1—O5	91.0(4)
Cu1—O5	2.62(1)	O2—Cu1—O2	180.0(5)

using a cotton diffusion layer. The solution of MnC_2O_4 and an appropriate nitrogen ligand were located at the bottom of this test-tube, followed by the layer of cotton. This layer had two functions: primarily it separates the two solutions (at the bottom and at the top) and exists as a diffusion layer. After the cotton layer was located in the test-tube, the solution of $\text{K}_2[\text{Cu}(\text{CN})_3]$ was pipetted. Subsequently, the test-tube was covered with parafilm. After several months, crystals of **1**, **2**, and **3** suitable for X-ray analysis were obtained. They were created at the bottom of the individual test-tubes. In this environment, the crystals had a long time to form and grow.

Subsequently it was decided to prepare compound **1** again, but faster than previously. MnC_2O_4 (0.343 mmol) and 2-methylimidazole (0.341 mmol) were dissolved in H_2O with methanol (25 mL + 25 mL) and were added to an Erlenmeyer flask. To the stirred solution, $\text{K}_2[\text{Cu}(\text{CN})_3]$ (0.114 mmol) was added. The solution was stirred for 6 h at ambient temperature. Next, the solution was filtered into a beaker to remove any solid particles. Complexes **4** and

5 were obtained by a slow evaporation of the solution as a mixture of a small amount of blue (**4**) and light blue (**5**) well-formed single crystals suitable for the X-ray crystal structure analysis. To obtain pure complexes, the preparation conditions were altered as follows: MnC_2O_4 (0.343 mmol), 2-methylimidazole (0.341 mmol), and $\text{K}_2[\text{Cu}(\text{CN})_3]$ (0.114 mmol) were dissolved in the solution of water and methanol in individual beakers to obtain saturated solutions. These solutions were mixed together and the resultant solution was filtered. By this procedure, only the pure complex **4** was prepared. In effect, the very small amount of complex **5** was why the infrared spectrum is not discussed here. Fortunately, this compound was prepared previously, so the crystallographic data can be compared with the previous information.

A solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.501 mmol) in 5 mL of water was combined with MnC_2O_4 (1.502 mmol) in 5 mL of water and with *N*-benzylimidazole (1.502 mmol) in the presence of H_2O and methanol. The blue powder of **6** was separated by filtration and dried at ambient temperature.

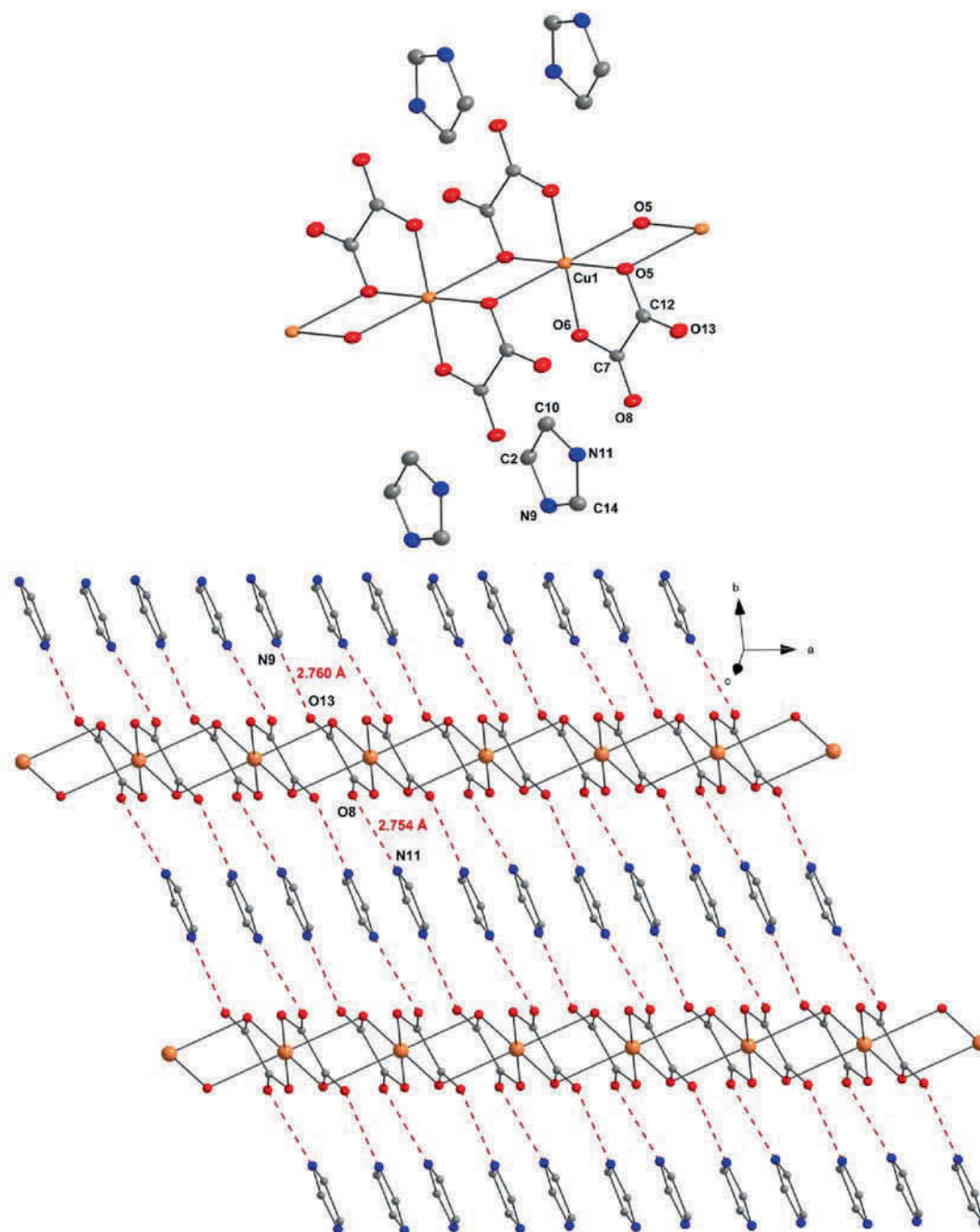


Fig. 2. DIAMOND drawing of $\{(Hiz)_2[Cu(ox)_2]\}_n$ (**2**) with atom numbering scheme. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are removed for clarity. Below: H-bond contacts between donor atom and acceptor atom (red dashed lines). Symmetry operations: (i) x, y, z ; (ii) $-x, -y, -z$.

Results and discussion

The Cu(II) ions in the one-dimensional polymeric chains **1** adopted an octahedral arrangement with the oxalate anions, coordinated in a tridentate manner through oxygen atoms. Each Cu(II) coordinates the same O6 donor set (Fig. 1). The basal plane is made up of four oxygen atoms of $C_2O_4^{2-}$ (Cu1—O3: 1.936(1) Å and Cu1—O4: 1.927(1) Å, Table 2) and the apical site is also occupied by two oxygen atoms of oxalate anions (Cu1—O5: 2.648(1) Å, semi-coordination). The

Jahn–Teller effect is responsible for the distortion of **1**. A packing diagram of compound **1** is shown in Fig. 1. The copper complex $\{K_2[Cu(ox)_2]\}_n$ (**1**) crystallises in the monoclinic space group $P2_1/c$ with two formula units in a cell of the following dimensions: $a = 4.8800(2)$ Å, $b = 6.6520(3)$ Å, $c = 13.5020(4)$ Å, $\beta = 104.499(3)^\circ$.

The bridging nature of the $C_2O_4^{2-}$ ion in **2** led to formation of the one-dimensional polymeric chain (Fig. 2). An O6 donor set (Cu1—O5: 1.934(2) Å and Cu1—O6: 1.928(2) Å, Table 2) is coordinated to the

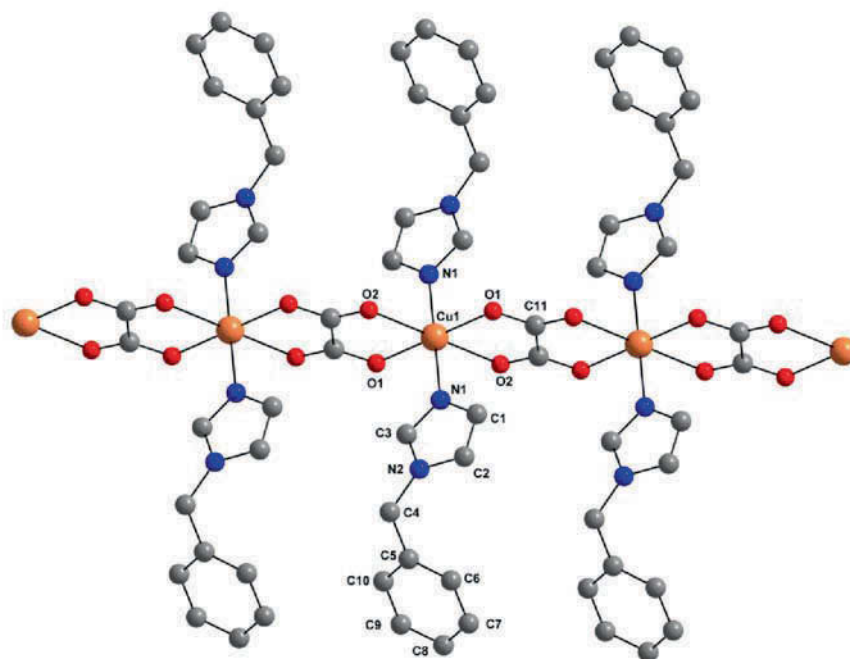


Fig. 3. DIAMOND drawing of $\{[\text{Cu}(\text{ox})(\text{N-BzIiz})_2]\}_n$ (**3**) with atom numbering scheme of asymmetric unit. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are removed for clarity. Symmetry operations: (i) x, y, z ; (ii) $-x, y + 1/2, -z + 1/2$; (iii) $-x, -y, -z$; (iv) $x, -y + 1/2, z + 1/2$.

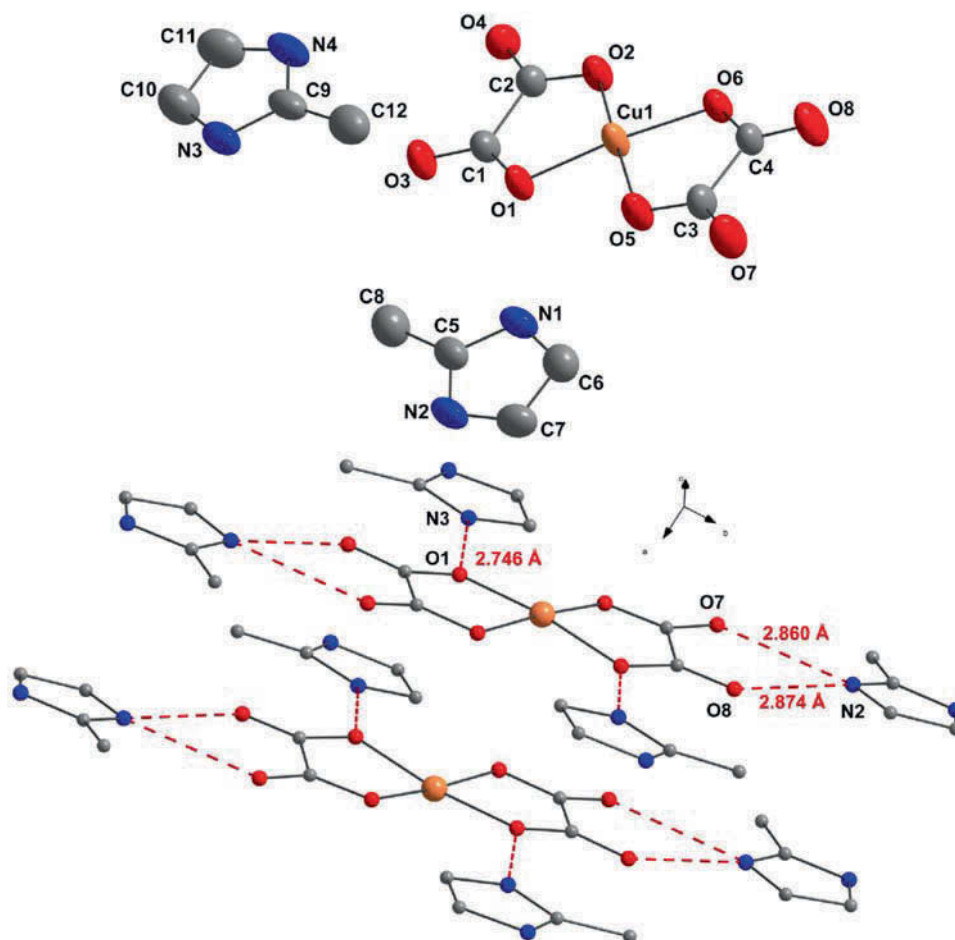


Fig. 4. DIAMOND drawing of $(\text{HMeiz})_2[\text{Cu}(\text{ox})_2]$ (**4**) with atom numbering scheme. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are removed for clarity. Below: H-bond contacts (red dashed lines). Symmetry operations: (i) x, y, z ; (ii) $-x, y, -z + 1/2$; (iii) $-x, -y, -z$; (iv) $x, -y, z + 1/2$; (v) $x + 1/2, y + 1/2, z$; (vi) $-x + 1/2, y + 1/2, -z + 1/2$; (vii) $-x + 1/2, -y + 1/2, -z$; (viii) $x + 1/2, -y + 1/2, z + 1/2$.

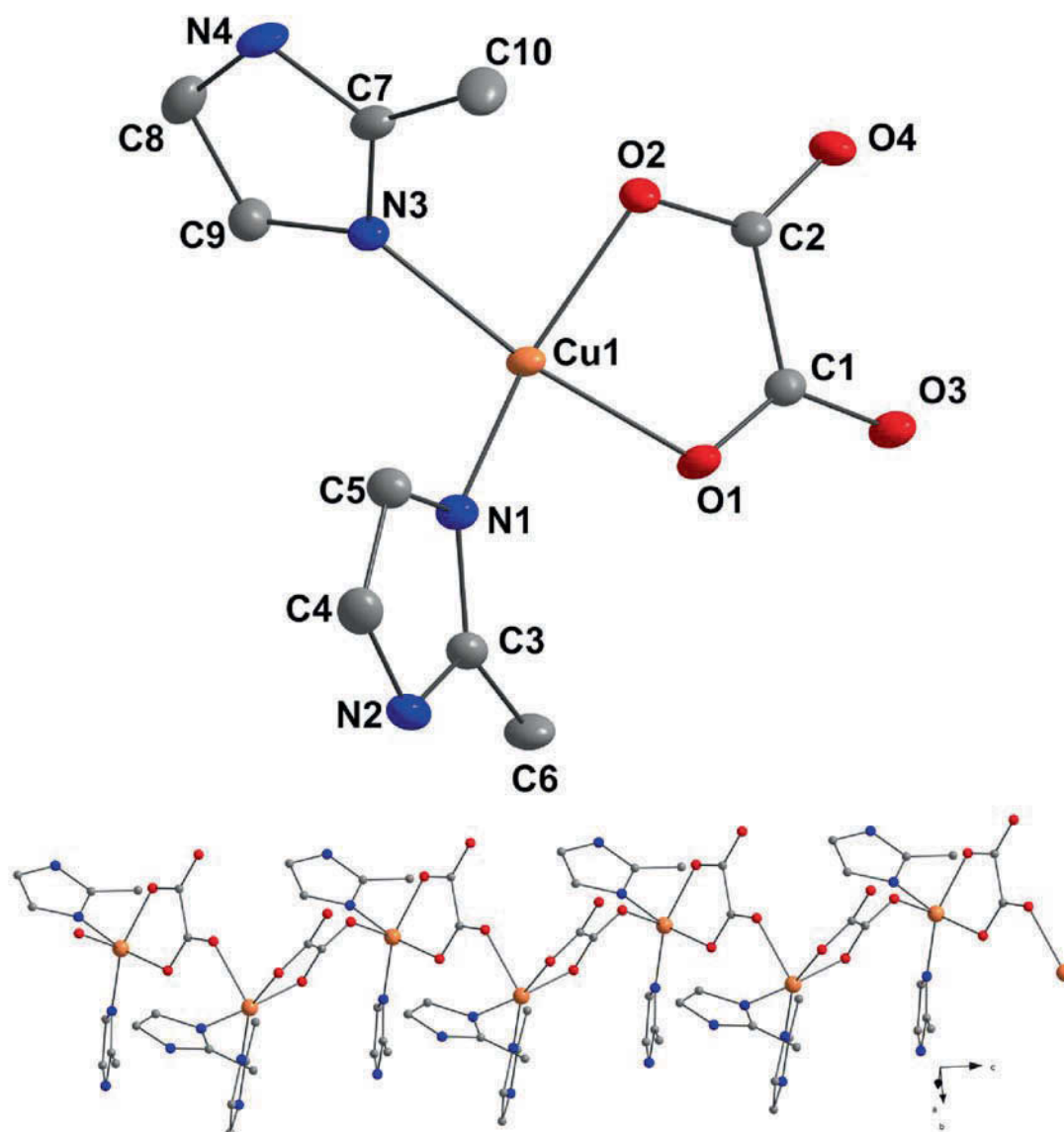


Fig. 5. DIAMOND drawing of asymmetric unit of $\{[\text{Cu}(\text{ox})(\text{Meiz})_2]\}_n$ (**5**) with atom numbering scheme. Thermal ellipsoids are drawn at 50 % probability level. Middle diagram: expansion chain of complex **5**. Hydrogen atoms are removed for clarity. Below: H-bond contacts (red dashed lines). Symmetry operations: (i) x, y, z ; (ii) $-x + 1/2, y, z + 1/2$; (iii) $x + 1/2, -y, z$; (iv) $-x, -y, z + 1/2$.

Cu(II) ion. Both O6 oxygen atoms are coordinated in a monodentate fashion to Cu(II), while the four O5 oxygen atoms created a chelating mode of bridging. This system contains intermolecular hydrogen bonds between O13 (O8) oxygen from the oxalate group and N9 (N11) nitrogen from the imidazolium cationic part (donor–acceptor distances: 2.760 Å and 2.754 Å, Fig. 2). The compound $\{(\text{Hiz})_2[\text{Cu}(\text{ox})_2]\}_n$ (**2**) crystallises in the triclinic space group P-1 with $Z = 1$ in a cell having the dimensions of: $a = 3.6170(2)$ Å, $b = 9.4000(6)$ Å, $c = 10.0230(11)$ Å, $\alpha = 106.617(6)^\circ$, $\beta = 97.164(6)^\circ$, $\gamma = 94.486(5)^\circ$.

A recent study of **2** indicated the complex to be very similar to the compound as prepared. For example, Chattopadhyay et al. (1995) achieved the fol-

lowing cell lengths: $a = 3.669(1)$ Å, $b = 9.422(8)$ Å, $c = 10.074(2)$ Å and cell angles $\alpha = 106.81(2)^\circ$, $\beta = 97.77(2)^\circ$, $\gamma = 94.02(2)^\circ$ in comparison with the present data. The differences between the previous and current data in cell volume (328.15(11) Å³; 321.67(4) Å³), density (1.912 g cm⁻³; 1.950 g cm⁻³), and goodness of fitting (2.76; 1.115) are also evident. Unfortunately, the temperature of measurements was not given in the 1995 article. In the present study, a low temperature measurement was made at 150(2) K. The complex (Chattopadhyay et al., 1995) was prepared as follows: to a suspension of 1.5 g of copper oxalate in 150 mL distilled water, approximately 3 g of oxalic acid was added. The solution was heated in a water bath for 45 min then, 1.15 g of imidazole was

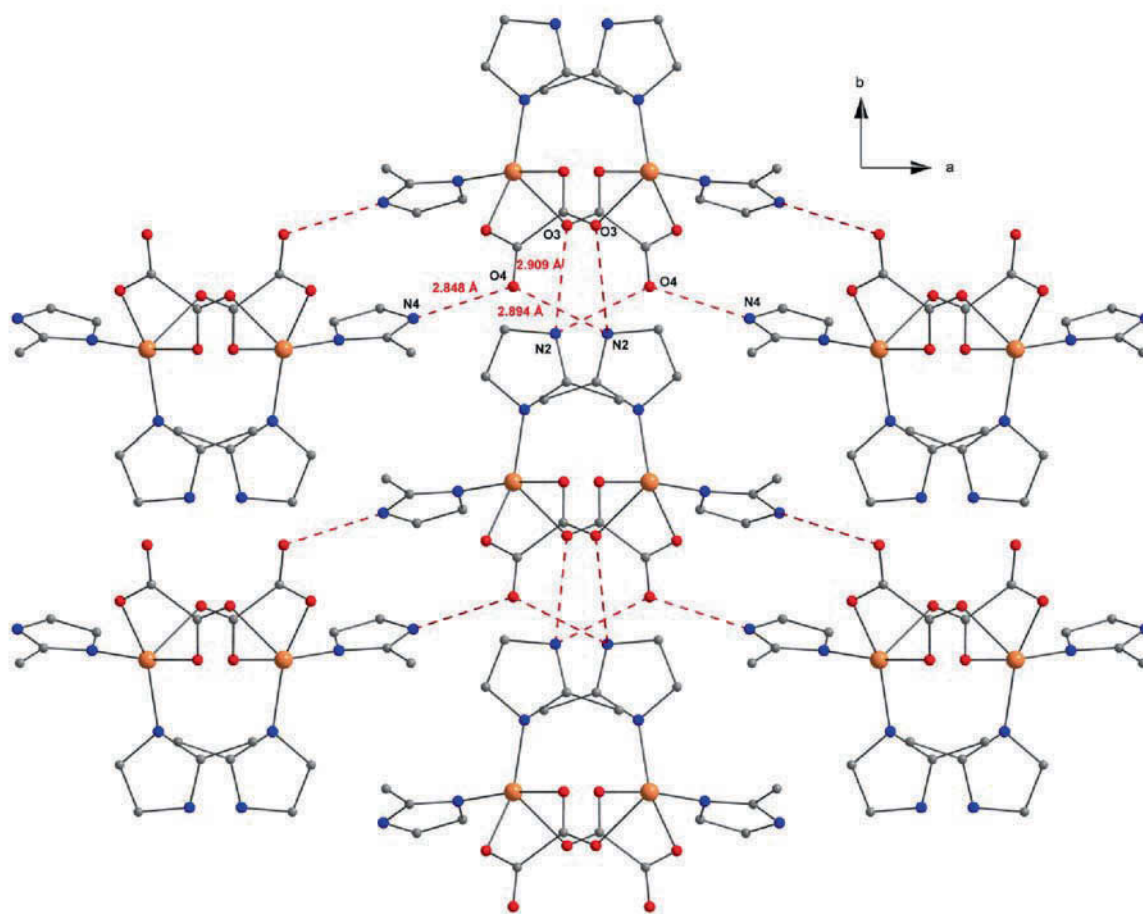


Fig. 6. DIAMOND drawing of $[\text{Cu}(\text{Hox})_2(\text{H}_2\text{O})_2](\text{N-Bzliz})$ (**6**) with atom numbering scheme. Thermal ellipsoids are drawn at 50 % probability level. Hydrogen atoms are removed for clarity. Below: H-bond contacts (red dashed lines). Symmetry operations: (i) x, y, z ; (ii) $-x + 1/2, y + 1/2, -z$; (iii) $-x, -y, -z$; (iv) $x + 1/2, -y + 1/2, z$.

slowly added. After heating in a water bath, it was filtered hot. The present copper(II) complex **2** was prepared by an alternative test-tube route (see Experimental).

The X-ray crystal structure of **3** also revealed a one-dimensional linear polymeric chain (Fig. 3). The oxalate dianion bridges in a bis-bidentate fashion between the two Cu(II) ions (Cu1—O1: 1.977(1) Å and Cu1—O2: 2.375(1) Å, Table 2), the remaining two coordination sites are occupied by nitrogen atoms of *N*-benzylimidazole (Cu1—N1: 2.030(1) Å). $\{[\text{Cu}(\text{ox})(\text{N-Bzliz})_2]\}_n$ (**3**) crystallises in the monoclinic system, space group $P2_1/c$ ($a = 5.6080(2)$ Å, $b = 7.7360(7)$ Å, $c = 22.985(1)$ Å, $\beta = 103.409(4)^\circ$, $Z = 2$).

In compound **4**, the Cu(II) centres exhibit a slightly distorted square-planar geometry. Copper(II) is four-coordinated in a square planar arrangement defined by four oxalate oxygen atoms (four monodentate oxygen atoms: Cu1—O1: 1.912(6) Å; Cu1—O2: 1.943(4) Å; Cu1—O3: 1.956(6) Å; and Cu1—O4: 1.924(4) Å, Table 2). The structure of **4** consists of a coordination anion $[\text{Cu}(\text{ox})_2]^{2-}$ and 2-methylimidazolium cations (Fig. 4). In addition, com-

Table 3. Compounds and corresponding chromophores

Compound ^a	Chromophore
$\{\text{K}_2[\text{Cu}(\text{ox})_2]\}_n$ (1)	$\text{Cu}_1\text{O}_2\text{O}'_2\text{O}''_2$
$\{(\text{Hiz})_2[\text{Cu}(\text{ox})_2]\}_n$ (2)	$\text{Cu}_1\text{O}_4\text{O}'_2$
$\{[\text{Cu}(\text{ox})(\text{N-Bzliz})_2]\}_n$ (3)	$\text{Cu}_1\text{O}_2\text{O}'_2\text{N}_2$
$(\text{HMeiz})_2[\text{Cu}(\text{ox})_2]$ (4)	$\text{Cu}_1\text{OO}'\text{O}''\text{O}'''$
$\{[\text{Cu}(\text{ox})(\text{Meiz})_2]\}_n$ (5)	$\text{Cu}_1\text{OO}'\text{O}''\text{NN}'$
$[\text{Cu}(\text{Hox})_2(\text{H}_2\text{O})_2](\text{N-Bzliz})$ (6)	$\text{Cu}_1\text{O}_2\text{O}'_2\text{O}''_2$

^a) ox = oxalate ion, iz = imidazole, N-Bzliz = *N*-benzylimidazole, Meiz = 2-methylimidazole.

ound **4** exhibits intermolecular H-bonding between the oxygen atoms of the oxalate group (O1, O7, and O8 atoms) and nitrogen of 2-methylimidazolium. The corresponding distances are shown in Fig. 4. $(\text{HMeiz})_2[\text{Cu}(\text{ox})_2]$ (**4**) crystallises in the monoclinic system, space group $C2/c$ ($a = 15.80(5)$ Å, $b = 19.062(1)$ Å, $c = 14.319(6)$ Å, $\beta = 117.09(6)^\circ$, $Z = 8$).

The coordination environment of the Cu(II) ion in **5** is square-pyramidal in which two equatorial

sites are occupied by the nitrogen atoms of the 2-methylimidazole and the remaining two sites are occupied by two oxygen atoms of the $C_2O_4^{2-}$ anion and the apical site is occupied by one oxygen atom of the oxalate anion (Cu1—O1: 1.968(4) Å; Cu1—O2: 1.992(5) Å; Cu1—N1: 1.971(6) Å; Cu1—N4: 1.977(6) Å; and Cu1—O3: 2.257(5) Å, Table 2). Two copper(II) ions are bridged by two oxygen atoms (O1 and O3) of one oxalate ion (Fig. 5). The compound $\{[Cu(ox)(Meiz)_2]\}_n$ (**5**) crystallises in the orthorhombic space group $Pca2_1$.

The structure of this complex was previously detailed in the literature. The authors prepared this complex in 1987 and the crystal structure was determined at ambient temperature (293 ± 2) K. The present study included a low temperature measurement at 100(1) K, hence, differences exist between the two studies. For example, the space group, cell parameters, volume, and density of $\{[Cu(ox)(Meiz)_2]\}_n$ (Geiser et al., 1987) are $Pbc2_1$, $a = 8.235(2)$ Å, $b = 19.565(5)$ Å, $c = 7.994(2)$ Å, $V = 1288.07$ Å³, $\rho_{calc} = 1.63$ g cm⁻³. In the present study, the crystal structure of $\{[Cu(ox)(Meiz)_2]\}_n$ has the following characteristics: $Pca2_1$, $a = 19.4407(5)$ Å, $b = 8.2161(2)$ Å, $c = 7.8900(2)$ Å, $V = 1260.25(5)$ Å³, $\rho_{calc} = 1.664$ g cm⁻³. The complex (Geiser et al., 1987) was formed by the slow evaporation of an aqueous solution containing $Cu(CH_3CO_2)_2 \cdot H_2O$ and 2-methylimidazole and $Na_2C_2O_4$, affording dark blue crystals. The present alternative synthetic method is based on a test-tube experiment (see Experimental).

X-ray analysis of the blue powder confirmed an oxalate-bridged copper(II) structure **6**. The structure of **6** is shown in Fig. 6. The Cu(II) ion is surrounded by six oxygen atoms. The basal plane is made up of four oxygen atoms of $C_2O_4^{2-}$ (Cu1—O2: 1.92(1) Å and Cu1—O3: 1.96(1) Å, Table 2) and the apical site is occupied by two oxygen atoms of water molecules (Cu1—O5: 2.62(1) Å, semi-coordination). The axial bonds are longer than the equatorial bonds due to the Jahn–Teller effect. The structure also consists of a *N*-benzylimidazolium cation. This system contains intermolecular hydrogen bonds between the oxygen of the oxalate group and the water molecule (donor-acceptor distance: 2.650 Å). The last copper complex $[Cu(Hox)_2(H_2O)_2](N-BzIiz)$ (**6**) crystallises in the monoclinic system, space group $P2_1/a$ ($a = 10.9164(3)$ Å, $b = 11.1727(3)$ Å, $c = 10.7713(3)$ Å, $\beta = 104.836(3)^\circ$, $Z = 2$).

The composition and properties of the corresponding products are summarised in Tables 1–4.

Conclusions

This study presents the syntheses and crystal structures of six copper(II) compounds. By using the $C_2O_4^{2-}$ anion, it was possible to successfully synthesise $\{K_2[Cu(ox)_2]\}_n$ (**1**), $\{(Hiz)_2[Cu(ox)_2]\}_n$ (**2**),

Table 4. Infrared spectra for complexes **1**, **2**, **3**, **4**, and **6**

	$\{K_2[Cu(ox)_2]\}_n$ (1)	$\{(Hiz)_2[Cu(ox)_2]\}_n$ (2)	$\{[Cu(ox)(N-BzIiz)_2]\}_n$ (3)	$(HMeiz)_2[Cu(ox)_2]$ (4)	$[Cu(Hox)_2(H_2O)_2](N-BzIiz)$ (6)
$\nu_a(COO^-)$	1670vs, 1636vs	1660vs, 1633vs	1613vs	1666 vs, 1634 vs	1650vs 1624vs
$\nu_s(COO^-)$	1404s	1410s	1398m	1404s	1438m
$\nu_s(CO) + \delta(O-C=O)$	1277s	1281s	1282s	1276s	1300m, 1287m
$\nu_s(CO) + \delta(O-C=O)$	894m	889m	862w	919m	892m
$\delta(O-C=O) + \nu(MO)$	788s	796s	797m	786s	724s
$\nu(MO) + \nu(CC)$	552m	554m	575w	552m	536w
$\delta(\text{ring}) + \delta(O-C=O)$	488s	503m	496m	487s	494w

$\{[\text{Cu}(\text{ox})(\text{N-BzIiz})_2]\}_n$ (**3**), $(\text{HMeiz})_2[\text{Cu}(\text{ox})_2]$ (**4**), $\{[\text{Cu}(\text{ox})(\text{Meiz})_2]\}_n$ (**5**), and $[\text{Cu}(\text{Hox})_2(\text{H}_2\text{O})_2](\text{N-BzIiz})$ (**6**), where ox = oxalate ion, iz = imidazole, N-BzIiz = N-benzylimidazole, Meiz = 2-methylimidazole. The present study also reveals that the replacement of imidazole by 2-methylimidazole or N-benzylimidazole can cause a significant change in the molecular structures and chromophores, as shown in Table 3. Hence, the role of the nitrogen ligand and the bridging mode of the $\text{C}_2\text{O}_4^{2-}$ anion is clearly evident.

The coordination polyhedron in structures **1**, **2**, **3**, and **6** is octahedral with a central atom in the centre of the symmetry. The square-planar coordination of the copper(II) central atom in **4** is provided by four oxygen donor atoms of the oxalate chelating ligand. In **5**, the Cu(II) atom is penta-coordinated by the three donor oxygen atoms of the oxalate groups and the remaining two sites are occupied by the nitrogen atoms of the 2-methylimidazole.

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References

- Akhrif, Y., Server-Carrió, J., Sancho, A., García-Lozano, J., Escrivá, E., Folgado, J. V., & Soto, L. (1999). Synthesis, crystal structure, and magnetic properties of oxalato-copper(II) complexes with 3,3-bis(2-imidazolyl)propionic acid, an imidazole-carboxylate polyfunctional ligand: From mononuclear entities to ladder-like chains. *Inorganic Chemistry*, *38*, 1174–1185. DOI: 10.1021/ic980982x.
- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K., & Watkin, D. J. (2003). CRYSTALS version 12: software for guided crystal structure analysis. *Journal of Applied Crystallography*, *36*, 1487. DOI: 10.1107/s0021889803021800.
- Boultif, A., & Lour, D. (2004). Powder pattern indexing with the dichotomy method. *Journal of Applied Crystallography*, *37*, 724–731. DOI: 10.1107/s0021889804014876.
- Brandenburg, K., & Putz, H. (2015). Diamond: Crystal and molecular structure visualization [computer software]. Bonn, Germany: Crystal Impact GbR.
- Bruker AXS Inc. (2001). SADABS [computer software]. Madison, WI, USA: Bruker AXS Inc.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Mallamo, M., Mazzzone, A., Polidori, G., & Spagna, R. (2012). SIR2011: a new package for crystal structure determination and refinement. *Journal of Applied Crystallography*, *45*, 357–361. DOI: 10.1107/s0021889812001124.
- Chattopadhyay, S. K., Mak, T. C. W., Luo, B. S., Thompson, L. K., Rana, A., & Ghosh, S. (1995). Synthesis, structural and magnetic studies of imidazolium bis(oxalato)cuprate(II). *Polyhedron*, *14*, 3661–3667. DOI: 10.1016/0277-5387(95)00151-h.
- Chen, W., Chu, J. F., Mutikainen, I., Reedijk, J., Turpeinen, U., & Song, Y. F. (2011). Tripodal bis(imidazole)-based ligands and their chelation to copper(II). *CrystEngComm*, *13*, 7299–7304. DOI: 10.1039/c1ce05556a.
- Deacon, G. B., & Phillips, R. J. (1980). Relationship between the carbon-oxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination. *Coordination Chemistry Reviews*, *33*, 227–250. DOI: 10.1016/s0010-8545(00)80455-5.
- Duan, Z. M., Zhang, Y., Zhang, B., & Zhu, D. B. (2008). $\text{Co}(\text{C}_2\text{O}_4)(\text{HO}(\text{CH}_2)_3\text{OH})$: An antiferromagnetic neutral zigzag chain compound showing long-range ordering of spin canting. *Inorganic Chemistry*, *47*, 9152–9154. DOI: 10.1021/ic801544r.
- Favre-Nicolin, V., & Černý, R. (2002). FOX, ‘free objects for crystallography’: a modular approach to *ab initio* structure determination from powder diffraction. *Journal of Applied Crystallography*, *35*, 734–743. DOI: 10.1107/s0021889802015236.
- Geiser, U., Ramakrishna, B. L., Willett, R. D., Hulsbergen, F. B., & Reedijk, J. (1987). Crystal structures and magnetic behavior of pyridinium bis(oxalato)cuprate(II)-oxalic acid and bis(2-methylimidazole)copper(II) oxalate. *Inorganic Chemistry*, *26*, 3750–3756. DOI: 10.1021/ic00269a026.
- Halcrow, M. A. (2013). Jahn–Teller distortions in transition metal compounds, and their importance in functional molecular and inorganic materials. *Chemical Society Reviews*, *42*, 1784–1795. DOI: 10.1039/c2cs35253b.
- Jin, Z. N., & Lin, H. (2011). Poly[diimidazole- μ_4 -oxalato- μ_2 -oxalato-dicopper(II)]. *Acta Crystallographica Section E: Structure Reports Online*, *67*, m680, DOI: 10.1107/s1600536811015777.
- Julve, M., Verdager, M., Gleizes, A., Philoche-Lavisalles, M., & Kahn, O. (1984). Design of μ -oxalato copper(II) binuclear complexes exhibiting expected magnetic properties. *Inorganic Chemistry*, *23*, 3808–3818. DOI: 10.1021/ic00191a028.
- Kang, D. B. (2005). Influence of Jahn–Teller distortion on the magnetic coupling in oxalato-bridged copper(II) dimers: An orbital interpretation of the superexchange mechanism. *Bulletin of the Korean Chemical Society*, *26*, 1965–1968. DOI: 10.5012/bkcs.2005.26.12.1965.
- Kaşaş, G., Paşaoğlu, H., & Karabulut, B. (2011). Magnetic, structural and computational studies on transition metal complexes of a neurotransmitter, histamine. *Journal of Molecular Structure*, *1000*, 39–48. DOI: 10.1016/j.molstruc.2011.05.047.
- Kuchár, J., Černák, J., Sabová, I., Kappenstein, C., Kajňáková, M., Orendáč, M., & Boča, R. (2009). Cu–Ni hetero-bimetallic compounds, Part 1: Preparation, structure and properties of $[\text{Cu}_{0.05}\text{Ni}_{0.95}(\text{bpy})_2(\text{ox})]\cdot 4\text{H}_2\text{O}$. *Solid State Sciences*, *11*, 950–955. DOI: 10.1016/j.solidstatesciences.2008.03.032.
- Leong, W. L., & Vittal, J. J. (2011). Synthesis, characterization and structures of copper(II) complexes containing carboxylate and sulfonate groups. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, *71*, 557–566. DOI: 10.1007/s10847-011-0015-6.
- Matelková, K., Mašlejová, A., & Moncoř, J. (2013). Various modes of oxalato ligand in copper(II) complexes. In M. Melnik, P. Segla, & M. Tatarko (Eds.), *Recent developments in coordination, bioinorganic and applied inorganic chemistry* (pp. 288–293). Bratislava, Slovakia: Slovak University of Technology Press.
- Meng, W. L., Liu, G. X., & Okamura, T. a., Kawaguchi, H., Zhang, Z. H., Sun, W. Y., & Ueyama, N. (2006). Syntheses, crystal structures, and magnetic properties of novel copper(II) complexes with the flexible bidentate ligand 1-bromo-3,5-bis(imidazol-1-ylmethyl)benzene. *Crystal Growth & Design*, *6*, 2092–2102. DOI: 10.1021/cg060304i.
- Murphy, B., & Hathaway, B. (2003). The stereochemistry of the copper(II) ion in the solid-state—some recent perspectives linking the Jahn–Teller effect, vibronic coupling, structure correlation analysis, structural pathways and comparative X-ray crystallography. *Coordination Chemistry Reviews*, *243*, 237–262. DOI: 10.1016/s0010-8545(03)00084-5.

- Oxford Diffraction Ltd. (2013). CrysAlis RED, CrysAlis CCD, Version 1.171.36.32 [computer software]. Abingdon, UK: Oxford Diffraction Ltd.
- Petříček, V., Dušek, M., & Palatinus, L. (2014). Crystallographic computing system JANA2006: General features. *Zeitschrift für Kristallographie*, 229, 345–352. DOI: 10.1515/zkri-2014-1737.
- Sánchez, H., Server-Carrió, J., Escrivà, E., Soto, L., García-Lozano, J., Sancho, A., & Ramírez de Arellano, C. (2013). Mononuclear and binuclear copper(II) complexes with bis(2-imidazolyl)(bis(methoxycarbonyl)methylmethane) (BIBM), a tripodal bis(imidazole) based ligand. Synthesis, crystal structure and magnetic characterization of [Cu(BIBM)₂](ClO₄)₂ and [{Cu(BIBM)(H₂O)}₂(μ_{1,2,3,4}-C₂O₄)](C₄O₄) · 6H₂O. *Polyhedron*, 50, 383–389. DOI: 10.1016/j.poly.2012.11.024.
- Sheldrick, G. M. (2008). A short history of SHELX. *Acta Crystallographica Section A*, A64, 112–122. DOI: 10.1107/s0108767307043930.
- Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Crystallographica Section C*, C71, 3–8. DOI: 10.1107/s2053229614024218.
- Spek, A. L. (2015). PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallographica Section C*, C71, 9–18. DOI: 10.1107/s2053229614024929.
- Toby, B. H. (2005). CMPR – a powder diffraction toolkit. *Journal of Applied Crystallography*, 38, 1040–1041. DOI: 10.1107/s0021889805030232.
- Xu, Q. A. (2011). catena-Poly[[bis(1-ethyl-1*H*-imidazole-κ*N*³)copper(II)]-μ-oxalato-κ⁴O¹, O² : O¹, O²']. *Acta Crystallographica Section E: Structure Reports Online*, 67, m1585. DOI: 10.1107/s1600536811043121.
- Zhu, Q. R., & Zhang, W. (2013). Synthesis, structural and dielectric characterization of two imidazole- and oxalate-containing copper(II) complexes. *Zeitschrift für Anorganische und Allgemeine Chemie*, 639, 1274–1278. DOI: 10.1002/zaac.201300101.