# Synthesis, X-ray Crystal Structure and Magnetic Properties of Oxalato-Bridged Copper(II) Complexes with 2,3-Bis(2-pyridyl)pyrazine, 2,3-Bis(2-pyridyl)quinoxaline and 2,2′-Bipyrazine as Peripheral Ligands

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Five oxalate-containing copper(II) complexes of formula $[Cu(dpq)(H_2O)(ox)]\cdot 5H_2O$ (**1**), $[Cu(dpp)(H_2O)(ox)]\cdot H_2O$ (**2**), $[Cu(bpz)(ox)]_n$ (**3**), $[Cu_2(dpp)_2(H_2O)_2(NO_3)_2(ox)]\cdot 4H_2O$ (**4**) and $[Cu_2Cl_2(bpz)_2(H_2O)_2(ox)][Cu(bpz)(H_2O)_2(ox)]\cdot 2H_2O$ (**5**) [dpq = 2,3-bis(2-pyridyl)quinoxaline; dpp = 2,3-bis(2-pyridyl)-pyrazine; bpz = 2,2′-bipyrazine; ox = oxalate] were prepared and their structures were determined by X-ray diffraction on single crystals. Complexes **1** and **2** are discrete mononuclear complexes with oxalate and dpq (**1**)/dpp (**2**) acting as bidentate ligands. Complex **3** is a neutral oxalato-bridged (2,2′-bipyrazine)copper(II) chain where the oxalate adopts a bidentate/monodentate coordination mode, whereas **4** is an oxalato-bridged copper(II) dinuclear complex with ox and dpp acting as bis-bidentate and bidentate ligands, respectively. The structure of **5** contains neutral $[Cu(bpz)(H_2O)_2(ox)]$ (mononuclear) and $[Cu_2(bpz)_2(H_2O)_2Cl_2(ox)]$ (dinuclear) units where the bpz acts as a bidentate ligand and the oxalate group adopts the bidentate (mononuclear) and bis-bidentate (dinuclear) coordination modes. The copper atoms have distorted square pyramidal (**1** and **2**) and elongated octahedral (**3**–**5**) geometries: two nitrogen atoms from heterocyclic N-donors and two oxalate-oxygen atoms occupy the equatorial positions (**1**–**5**) and a water molecule (**1** and **2**), two oxalate-oxygen atoms (**3**), a water molecule and a nitrate-oxygen (**4**), and either two water molecules (**5**), mononuclear) or a chlorine atom and a water molecule (**5**, dinuclear) fill the axial ones. Magnetic susceptibility measurements for **3**–**5** in the temperature range 1.9–290 K reveal the occurrence of weak ($J$ = –1.4 $cm^{-1}$, **3**) and strong (–312 and –345 $cm^{-1}$ for **4** and **5**, respectively; $\hat{H} = -J\cdot\hat{S}_A\cdot\hat{S}_B$) antiferromagnetic interactions between the copper(II) atoms in agreement with the out-of-plane (**3**) and in-plane (**4** and **5**) exchange pathways involved.



## Introduction

An impressive amount of work has been devoted to magneto-structural studies of oxalato-bridged copper(II) complexes.[1−5] The four main reasons accounting for this continuous interest are: (i) the remarkable efficiency of the oxalate ligand (the dianion of oxalic acid $H_2ox$) to mediate strong magnetic interactions between copper(II) ions when adopting the bis-bidentate bridging mode (singlet-triplet energy gap up to $-386$ $cm^{-1}$ between a pair of copper(II) ions separated by more then 5.4 Å);[1,5] (ii) the copper(II) ion is the simplest case of magnetic exchange given that it corresponds to a doublet spin state without orbital contribution; (iii) the great plasticity of the coordination sphere of the copper(II) ion (four-, five- and six-coordinate geometries are commonly observed), which allows variations of the orientation and symmetry of the molecular orbital describing its unpaired electron (magnetic orbital) simply by changing the nature of the blocking N-donor ligand used;[1a,1c,1e] (iv) X-ray quality crystals which are commonly air- and moisture-stable can be obtained from aqueous solutions containing oxalate, copper(II) and organic ligands by slow evaporation of the solvent at room temperature.

The major synthetic problem chemists had to overcome when investigating the formation of discrete oxalate-containing copper(II) complexes is the formation of the insoluble, oxalato-bridged copper(II) chain $Cu(C_2O_4)\cdot$

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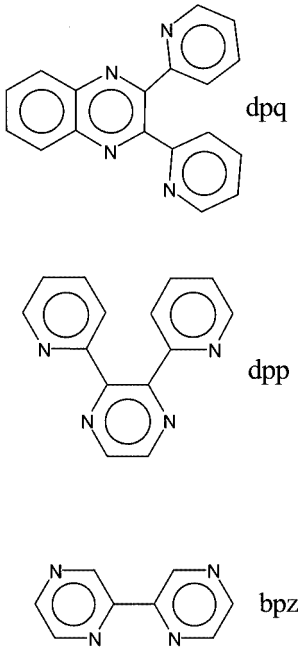
$1/3H_2O$.[3b,6] The formation of this chain is precluded in the presence of polydentate nitrogen-donor ligands (L) allowing the formation of mixed-ligand species [CuL(ox)], which, in turn, can be used as ligands in designing higher nuclearity species. Two representative examples of this versatility are $[Cu(tmen)(ox)\cdot 4H_2O]$ and $[Cu(terpy)(H_2O)(ox)]\cdot 4H_2O$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; terpy = 2,2′:6′,2′′-terpyridine).[1c,1e,7] The reaction of the former neutral mononuclear complex with the preformed species $[Cu(tmen)]^{2+}$ and $[Cu(dien)]^{2+}$ (dien = diethylenetriamine) in aqueous solution provides a direct route towards the centrosymmetric and asymmetric oxalato-bridged copper(II) complexes of formula $[Cu_2(tmen)_2(H_2O)_2(ox)](ClO_4)_2\cdot 1.25H_2O$ and $[Cu(dien)(ox)Cu(H_2O)_2(tmen)](ClO_4)_2$.[1c,1e] As for the terpy-containing precursor, its reaction with the partially blocked species $[Cu(terpy)]^{2+}$ and $[VO(ox)]\cdot 4H_2O$[8] affords the oxalato-bridged homo- and heterometallic compounds $[Cu_2(terpy)_2(H_2O)_2(ox)][Cu_2(terpy)_2(ox)](ClO_4)_4\cdot 2H_2O$ and $[Cu(terpy)(ox)VO(ox)(H_2O)]\cdot H_2O$.[7,9]

Following our previous magneto-structural works where the nitrogen heterocycles 2,2′-bipyridine (bipy),[1d,1i,1m,3g,10] 1,10-phenanthroline (phen),[1f,11] 2,2′-dipyridylamine (dpa)[1p] and 2,2′-bipyrimidine (bpym)[4a] were used as blocking ligands in the copper(II)-oxalate system, we tried to extend these studies to less-common nitrogen donors such as 2,3-bis(2-pyridyl)quinoxaline (dpq), 2,3-bis(2-pyridyl)pyrazine (dpp) and 2,2′-bipyrazine (bpz; Scheme 1). Our first attempts afforded the copper(II) complexes of formula $[Cu(dpq)(H_2O)(ox)]\cdot 5H_2O$ (**1**), $[Cu(dpp)(H_2O)(ox)]\cdot H_2O$ (**2**), $[Cu(bpz)(ox)]_n$ (**3**), $[Cu_2(dpp)_2(H_2O)_2((NO_3)_2(ox)]\cdot 4H_2O$ (**4**) and $[Cu_2(bpz)_2(H_2O)_2Cl_2(ox)][Cu(bpz)(H_2O)_2(ox)]\cdot 2H_2O$ (**5**). Their preparation, structural characterization and magnetic investigation are presented here.




Scheme 1

## Results and Discussion

### Short Description of the Synthesis

Compound **2** was synthesized by treating a suspension of copper(II) oxalate (insoluble) and the N-donor ligand (dpp). Preparations of complexes **1**, **3**, **4** and **5** were in each case accomplished by treating a common, soluble copper(II) salt with the chosen N-donor ligand, and subsequently adding a solution containing oxalate. The reaction medium was $H_2O$/EtOH in the cases of **1**, **2** and **4**, $H_2O$ in the case of **3** and **5**. For **1**, **2** and **4** the stoichiometric amounts of reactants used are reflected in the stoichiometry of the products; for **3** and **5** (L = bpz) deficiency and excess, respectively, of oxalate are present in the reaction mixture as compared to the products formed, the $Cu^{II}$/bpz/ox reactants ratios being 2:2:1 and 1.5:1.5:1, respectively.

### Description of the Structures

#### $[Cu(dpq)(H_2O)(ox)]\cdot 5H_2O$ (1)

The structure of compound **1** is composed of discrete, neutral $[Cu(ox)(H_2O)(dpq)]$ molecules (Figure 1) and water of hydration. The copper atom has a distorted square-pyramidal environment (tetragonality parameter $\tau = 0.17$),[12] binding equatorially to two oxalate oxygen atoms [1.9344(15) and 1.9677(14) Å for Cu−O] and two dpq nitrogen atoms [1.9718(17) and 2.1244(16) Å for Cu−N(pyridyl) and Cu−N(pyrazine), respectively]; a water molecule coordinates in the apical position [2.1867(15) Å for $Cu-O_w$]. The equatorial plane of copper is tetrahedrally distorted (maximum atomic deviation 0.092 Å), with the metal atom displaced by 0.234 Å from the best mean plane toward the apical ligand. The dihedral angle between the equatorial plane and the best plane through the oxalate group is 7.6°. The quinoxaline group makes dihedral angles of 12.9 and 58.2° with the coordinated and uncoordinated pyridyl rings, respectively.

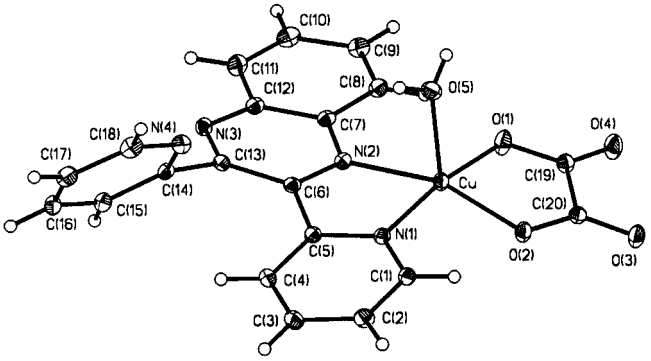



Figure 1. The complex unit $[Cu(dpq)(H_2O)(ox)]\cdot 5H_2O$ in compound **1**, showing the atomic numbering scheme; thermal ellipsoids are plotted at the 30% probability level

Centrosymmetrically related molecules are arranged in the crystals so as to give some overlap between the copper-

Table 1. Selected bond lengths (Å) and angles (°) for $[Cu(dpq)(H_2O)(ox)]\cdot 5H_2O$ (**1**)[a]

| | | | |
|---|---|---|---|
| Cu−O(1) | 1.9344(15) | Cu−N(2) | 2.1244(16) |
| Cu−O(2) | 1.9677(14) | Cu−O(5) | 2.1867(15) |
| Cu−N(1) | 1.9718(17) | | |
| O(1)−Cu−O(2) | 84.00(6) | N(1)−Cu−N(2) | 80.76(7) |
| O(1)−Cu−N(1) | 170.59(7) | O(1)−Cu−O(5) | 97.35(7) |
| O(2)−Cu−N(1) | 90.88(6) | O(2)−Cu−O(5) | 107.21(6) |
| O(1)−Cu−N(2) | 101.63(6) | N(1)−Cu−O(5) | 91.69(6) |
| O(2)−Cu−N(2) | 160.52(6) | N(2)−Cu−O(5) | 90.70(6) |
| O(1)−C(19) | 1.289(2) | O(4)−C(19) | 1.225(2) |
| O(2)−C(20) | 1.281(2) | C(19)−C(20) | 1.558(3) |
| O(3)−C(20) | 1.238(2) | | |
| C(19)−O(1)−Cu | 114.31(13) | O(1)−C(19)−C(20) | 113.90(17) |
| C(20)−O(2)−Cu | 113.20(13) | O(3)−C(20)−O(2) | 126.06(19) |
| O(4)−C(19)−O(1) | 126.1(2) | O(3)−C(20)−C(19) | 119.53(18) |
| O(4)−C(19)−C(20) | 120.03(18) | O(2)−C(20)−C(19) | 114.41(17) |
| N(1)−C(1) | 1.343(3) | C(6)−C(13) | 1.443(3) |
| N(1)−C(5) | 1.360(3) | C(7)−C(8) | 1.417(3) |
| N(2)−C(6) | 1.337(3) | C(7)−C(12) | 1.430(3) |
| N(2)−C(7) | 1.381(2) | C(8)−C(9) | 1.380(3) |
| N(3)−C(13) | 1.327(3) | C(9)−C(10) | 1.416(3) |
| N(3)−C(12) | 1.365(3) | C(10)−C(11) | 1.369(3) |
| N(4)−C(18) | 1.346(3) | C(11)−C(12) | 1.423(3) |
| N(4)−C(14) | 1.354(3) | C(13)−C(14) | 1.496(3) |
| C(1)−C(2) | 1.389(3) | C(14)−C(15) | 1.392(3) |
| C(2)−C(3) | 1.388(39 | C(15)−C(16) | 1.387(3) |
| C(3)−C(4) | 1.396(3) | C(16)−C(17) | 1.390(3) |
| C(4)−C(5) | 1.391(3) | C(17)−C(18) | 1.388(3) |
| C(5)−C(6) | 1.497(3) | | |
| C(1)−N(1)−C(5) | 119.54(17) | N(2)−C(7)−C(12) | 119.19(18) |
| C(1)−N(1)−Cu | 123.66(14) | C(8)−C(7)−C(12) | 119.22(18) |
| C(5)−N(1)−Cu | 116.70(13) | C(9)−C(8)−C(7) | 119.5(2) |
| C(6)−N(2)−C(7) | 118.86(179 | C(8)−C(9)−C(10) | 121.2(2) |
| C(6)−N(2)−Cu | 110.51(13) | C(11)−C(10)−C(9) | 120.58(19) |
| C(7)−N(2)−Cu | 129.53(13) | C(10)−C(11)−C(12) | 119.8(2) |
| C(13)−N(3)−C(12) | 118.55(17) | N(3)−C(12)−C(11) | 119.25(18) |
| C(18)−N(4)−C(14) | 117.04(18) | N(3)−C(12)−C(7) | 120.92(18) |
| N(1)−C81)−C82) | 122.04(19) | C(11)−C(12)−C(7) | 119.64(19) |
| C(3)−C(2)−C(1) | 118.87(19) | N(3)−C(13)−C(6) | 120.99(18) |
| C(2)−C(3)−C(4) | 119.2(29 | N(3)−C(13)−C(14) | 115.57(17) |
| C(5)−C(4)−C(3) | 119.14(19) | C(6)−C(13)−C(14) | 123.14(18) |
| N(1)−C(5)−C(4) | 121.00(18) | N(4)−C(14)−C(15) | 123.45(19) |
| N(1)−C(5)−C(6) | 113.71(17) | N(4)−C(14)−C(13) | 114.41(17) |
| C(4)−C(5)−C(6) | 125.26(18) | C(15)−C(14)−C(13) | 122.08(19) |
| N(2)−C(6)−C(13) | 120.45(18) | C(16)−C(15)−C(14) | 118.5(2) |
| N(2)−C(6)−C(5) | 116.39(17) | C(15)−C(16)−C(17) | 118.8(2) |
| C(13)−C(6)−C(5) | 123.15(17) | C(18)−C(17)−C(16) | 119.2(2) |
| N(2)−C(7)−C(8) | 121.59(18) | N(4)−C(18)−C(17) | 123.1(2) |

| D−H···A | D···A (Å) | H···A (Å) | D−H···A (°) |
|---|---|---|---|
| O(5)−H(51)···O(9) | 2.707(2) | 1.92 | 174 |
| O(5)−H(52)···O(10b) | 2.843(2) | 2.11 | 174 |
| O(6)−H(61)···O(7c) | 2.922(3) | 2.06 | 171 |
| O(6)−H(62)···O(8d) | 2.732(2) | 1.93 | 174 |
| O(7)−H(71)···O(6e) | 2.753(2) | 2.01 | 164 |
| O(7)−H(72)···N(3) | 3.029(2) | 2.31 | 171 |
| O(8)−H(81)···O(3f) | 2.886(2) | 2.17 | 162 |
| O(8)−H(82)···O(4) | 2.840(2) | 2.06 | 170 |
| O(9)−H(91)···O(10g) | 2.834(2) | 2.09 | 179 |
| O(9)−H(92)···O(7h) | 2.765(2) | 2.03 | 168 |
| O(10)−H(101)···N(4b) | 2.866(2) | 2.10 | 172 |
| O(10)−H(102)···O(3) | 2.781(2) | 1.99 | 172 |

[a] Symmetry transformations used to generate equivalent atoms: (b) $1-x, 1-y, -z$; (c) $1+x, y, z$; (d) $1+x, y, z-1$; (e) $1-x, -y, -1-z$; (f) $-x, 1-y, 1-z$; (g) $x, y-1, z$; (h) $-x, -y, -z$.

oxalate region of one molecule and the pyrazine ring of the other, the distances from individual pyrazine atoms to the oxalate plane ranging from 3.22 to 3.50 Å. This arrangement gives rise to the shortest metal···metal distance in the crystal [4.4193(5) Å for Cu···Cu(1a); (a) = $-x, 1-y, -z$], and also effectively screens the sixth coordination position of the copper atom, the Cu···N(2a) distance being 3.58 Å. There is additionally a slight π-π overlap between the benzo parts of the quinoxaline ligands of centrosymmetrically related molecules, the distances from the quinoxaline plane to three overlapping atoms ranging from 3.43 to 3.48 Å. The molecules are laced together through an extensive network of hydrogen bonds where oxalate, uncoordinated nitrogen and all water molecules are involved (see Table 1). The supramolecular arrangement features parallel sheets of molecules (Figure S1 in the Supporting Information).

The oxalate and dpq groups both coordinate in a monobidentate fashion, and thus have sites available for further metal binding. The bond lengths in the oxalate group are as typically found for this ligand in the didentate coordination mode, the C−O bonds of the coordinated oxygens [1.289(2) and 1.281(2) Å] being significantly longer than those of the uncoordinated ones [1.238(2) and 1.225(2) Å]. dpq is known to act as a chelate ligand either by forming a five-membered ring involving one pyridyl and one pyrazine nitrogen, or by forming a seven-membered ring involving the two pyridyl nitrogen atoms.[13,14] To the best of our knowledge, only two copper(II) complexes with unsubstituted dpq have been structurally characterized previously.[14] In one of these a seven-membered chelate ring was found[14a] and in the second ($[CuBr(dpq)]HSO_4\cdot$dpq) both chelate modes are present.[14b] In addition, the structures of two copper(II) complexes with methyl- or methoxy-substituted dpq (substitution at benzo carbon atoms) have been reported, and in both cases seven-membered chelate rings occur.[13h,15] Compound **1** is therefore the second example of a dpq-containing copper(II) complex with a five-membered chelate ring. It is noteworthy that the Cu−N(2)(pyrazine) bond length of 2.1244(16) Å is rather long for a copper−nitrogen bond in the equatorial plane of a square pyramid, and it is much longer than the Cu−N(1)(pyridyl) bond [1.9718(17) Å]. A similar feature was observed in $[CuBr(dpq)]HSO_4\cdot$dpq [2.101(8) vs. 2.016(8) Å].[14b] A certain difference in pyrazine and pyridyl Cu−N bond lengths is to be expected due to the weaker σ-donor strength of the pyrazine group.[13e] However, it is likely that steric effects also play a role in lengthening the Cu−N(pyrazine) bond in cases where the quinoxaline moiety is close to coplanar with the equatorial plane. In compound **1** this is indicated by the fact that the O(1)−Cu−N(2) angle of 101.63(6)° is much wider than the O(2)−Cu−N(1) angle of 90.88(6)°, possibly to make more room for the benzo part of the dpq ligand. A further indication of the steric effect is found when making a comparison with related dpp-containing copper(II) complexes where no benzo group is present. Studies of these compounds have shown that, although weak, axial bonds are often formed to the pyrazine nitrogen, presumably due to the weaker σ-donor strength mentioned above; the Cu−N(pyrazine) bond is comparable to, or only slightly longer than, the Cu−N(pyridyl) bond in cases where dpp chelates in two equatorial positions to a copper atom with square planar or square pyramidal geometry.[16] Analogous features have also been observed in

the copper(II) complexes of the more rigid pap ligand (pap = pyrazino[2,3-*f*][4,7]phenanthroline).[16b,17]

### [Cu(dpp)($H_2O$)(ox)]·$H_2O$ (2)

The structure of compound **2** consists of neutral, mononuclear [Cu(dpp)($H_2O$)(ox)] units (Figure 2) and water of hydration. The copper coordination sphere is square pyramidal with bidentate oxalate and dpp binding in the equatorial plane [1.941(2) and 1.953(2) Å for Cu−O and 1.988(2) and 1.989(2) Å for Cu−N] and a water molecule in the apical position [2.250(2) Å for Cu−$O_w$]. The mean equatorial plane of copper has a very slight tetrahedral distortion (maximum deviation 0.024 Å), and copper is displaced by 0.169 Å from this plane in the direction toward the apical oxygen atom. The oxalate group is essentially coplanar with the equatorial plane (dihedral angle 0.9°). The pyrazine ring makes a dihedral angle of 12.2° with the coordinated pyridyl ring, and a dihedral angle of 66.6° with the free pyridyl ring.

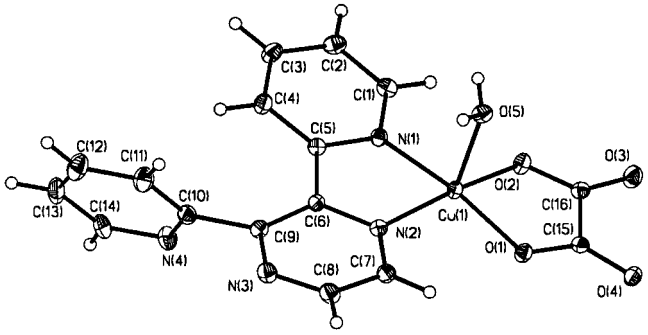



Figure 2. The complex unit [Cu(dpp)($H_2O$)(ox)] in compound **2** showing the atomic numbering scheme; thermal ellipsoids are plotted at the 30% probability level

In the crystal there is a slight π-π overlap between the oxalate group of the reference molecule and the coordinated pyridyl ring of a molecule displaced by the unit-cell translation along the *a* axis, with distances from the oxalate plane to the overlapping atoms being 3.30−3.42 Å. This arrangement also screens the sixth coordinating position of copper. There is also a slight π-π overlap between the uncoordinated and coordinated pyrazine of two molecules related by a screw-axis translation (3.46−3.62 Å). The complex molecules are connected by hydrogen bonds into a three-dimensional network: the coordinated water links neighbouring molecules to oxalate groups through hydrogen bonds, and the crystal water connects to pyridyl nitrogen atoms through hydrogen bonds (see Table 2 and Figure S2). The shortest intermolecular metal···metal distance is 5.911(1) Å [Cu(1)···Cu(1a); (a) = $-x$, $y - 0.5$, $2 - z$] and occurs between molecules connected by a hydrogen bond between coordinated water and oxalate oxygen.

The oxalate shows the typical features of bidentate bonding, with two long [1.281(4), 1.297(3) Å] and two short [1.218(3), 1.235(3) Å] C−O bonds. dpp bond lengths and angles compare well with previous findings.[16] The rotation of the uncoordinated pyridyl ring is also of a similar magnitude to that observed in other complexes with bidentate dpp.[16b,16e] In compound **2** the bonds from pyrazine and pyridyl nitrogen atoms to copper are comparable in length [1.982(2) and 1.988(2) Å, respectively], as has been observed earlier for equatorially coordinated, bidentate dpp,[16] but in contrast to the observation in **1** where the pyrazine ring is part of the quinoxaline moiety.

Table 2. Selected bond lengths (Å) and angles (°) for [Cu(dpp)($H_2O$)(ox)]·$H_2O$ (**2**)[a]

| | | | |
|---|---|---|---|
| Cu−O(2) | 1.941(2) | Cu−N(2) | 1.989(2) |
| Cu−O(1) | 1.953(2) | Cu−O(5) | 2.250(2) |
| Cu−N(1) | 1.988(2) | | |
| O(2)−Cu(1)−O(1) | 85.40(8) | N(1)−Cu(1)−N(2) | 81.02(9) |
| O(1)−Cu(1)−N(1) | 95.85(9) | O(2)−Cu(1)−O(5) | 97.88(8) |
| O(1)−Cu(1)−N(1) | 171.32(9) | O(1)−Cu(1)−O(5) | 91.85(8) |
| O(2)−Cu(1)−N(2) | 168.53(9) | N(1)−Cu(1)−O(5) | 96.48(8) |
| O(1)−Cu(1)−N(2) | 96.08(9) | N(2)−Cu(1)−O(5) | 93.44(9) |
| O(1)−C(15) | 1.281(4) | O(4)−C(15) | 1.235(3) |
| O(2)−C(16) | 1.297(3) | C(15)−C(16) | 1.565(4) |
| O(3)−C(16) | 1.218(3) | | |
| C(15)−O(1)−Cu(1) | 112.1(2) | O(1)−C(15)−C(16) | 115.3(2) |
| C(16)−O(2)−Cu(1) | 112.4(2) | O(3)−C(16)−O(2) | 125.6(3) |
| O(4)−C(15)−O(1) | 126.4(4) | O(3)−C(16)−C(15) | 120.4(2) |
| O(4)−C(15)−C(16) | 118.2(3) | O(2)−C(16)−C(15) | 114.0(2) |
| N(1)−C(1) | 1.345(4) | C(3)−C(4) | 1.385(4) |
| N(1)−C(5) | 1.365(4) | C(4)−C(5) | 1.389(3) |
| N(2)−C(7) | 1.338(4) | C(5)−C(6) | 1.497(4) |
| N(2)−C(6) | 1.348(3) | C(6)−C(9) | 1.407(4) |
| N(3)−C(8) | 1.334(4) | C(7)−C(8) | 1.390(4) |
| N(3)−C(9) | 1.352(4) | C(9)−C(10) | 1.500(4) |
| N(4)−C(10) | 1.341(4) | C(10)−C(11) | 1.390(4) |
| N(4)−C(14) | 1.354(4) | C(11)−C(12) | 1.390(5) |
| C(1)−C(2) | 1.386(4) | C(12)−C(13) | 1.384(6) |
| C(2)−C(3) | 1.390(4) | C(13)−C(14) | 1.381(5) |
| C(1)−N(1)−C(5) | 119.5(2) | N(2)−C(6)−C(9) | 119.4(2) |
| C(1)−N(1)−Cu(1) | 124.2(2) | N(2)−C(6)−C(5) | 114.0(2) |
| C(5)−N(1)−Cu(1) | 115.7(2) | C(9)−C(6)−C(5) | 126.6(2) |
| C(7)−N(2)−C(6) | 119.8(2) | N(2)−C(7)−C(8) | 119.7(3) |
| C(7)−N(2)−Cu(1) | 124.3(2) | N(3)−C(8)−C(7) | 121.9(3) |
| C(6)−N(2)−Cu(1) | 115.8(2) | N(3)−C(9)−C(6) | 120.6(2) |
| C(8)−N(3)−C(9) | 118.1(2) | N(3)−C(9)−C(10) | 115.2(2) |
| C(10)−N(4)−C(14) | 117.2(3) | C(6)−C(9)−C(10) | 124.1(2) |
| N(1)−C(1)−C(2) | 122.7(3) | N(4)−C(10)−C(11) | 123.0(3) |
| C(1)−C(2)−C(3) | 117.7(3) | N(4)−C(10)−C(9) | 115.9(3) |
| C(4)−C(3)−C(2) | 120.3(3) | C(11)−C(10)−C(9) | 121.1(3) |
| C(3)−C(4)−C(5) | 119.3(3) | C(10)−C(11)−C(12) | 118.5(3) |
| N(1)−C(5)−C(4) | 120.5(3) | C(13)−C(12)−C(11) | 119.5(3) |
| N(1)−C(5)−C(6) | 112.9(2) | C(14)−C(13)−C(12) | 118.0(3) |
| C(4)−C(5)−C(6) | 126.5(3) | N(4)−C(14)−C(13) | 123.7(3) |

| D−H···A | D···A (Å) | H···A (Å) | D−H···A (°) |
|---|---|---|---|
| O(5)−H(51)···O(4b) | 2.689(2) | 1.93 | 173 |
| O(5)−H(52)···O(2a) | 2.841(3) | 2.10 | 175 |
| O(6)−H(61)···N(4) | 2.899(4) | 1.94 | 162 |
| O(6)−H(62)···N(3c) | 2.969(4) | 2.03 | 166 |

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x$, $y - 0.5$, $2 - z$; (b) $x - 1$, $y$, $z$; (c) $-x$, $0.5 + y$, $1 - z$.

### [Cu(bpz)(ox)]$_n$ (3)

The structural building blocks in **3** are the neutral [Cu(bpz)(ox)] units. Both ox and bpz are bidentate ligands and they surround the copper atom in a close to square-planar geometry [1.9252(14) and 1.9258(15) Å for Cu−O and 1.9837(17) and 1.9869(16) Å for Cu−N]. Copper also has, however, two weak axial connections to semicoordinated oxalate oxygen atoms of centrosymmetrically related mol-

ecules [2.6170(18) and 2.7518(17) Å for Cu(1)−O(3a) and Cu(1)−O(1b); (a) = $-x$, $-y$, $-z$ and (b) = $1-x$, $-y$, $-z$] resulting in a 4+2 coordination sphere for copper, and formation of a chain with double out-of-plane oxalato bridges (Figure 3). The equatorial plane of copper has a moderate tetrahedral distortion (maximum atomic deviation 0.101 Å), the copper atom being displaced by only 0.004 Å from this plane toward O(3b). The dihedral angles between the equatorial plane and the oxalate and bpz planes are 12.8° and 5.3°, respectively.

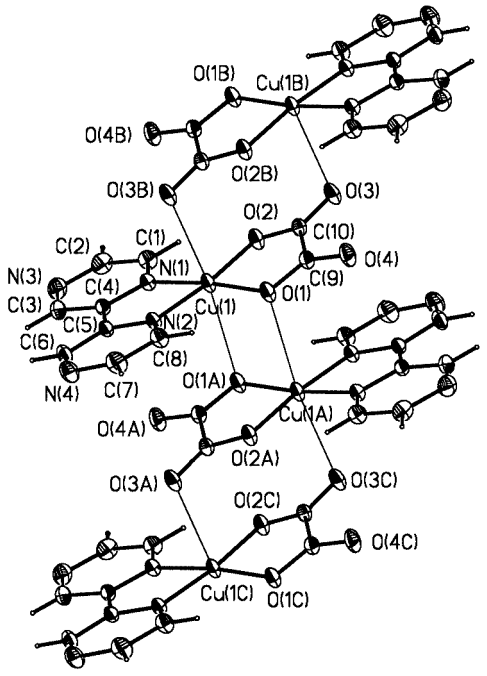



Figure 3. Section of the chain in $[Cu(bpz)(ox)]_n$ (**3**) showing the atomic numbering scheme; thermal ellipsoids are plotted at the 30% probability level; symmetry operations: (a) $1-x$, $-y$, $-z$; (b) $-x$, $-y$, $-z$; (c) $1+x$, $y$, $z$

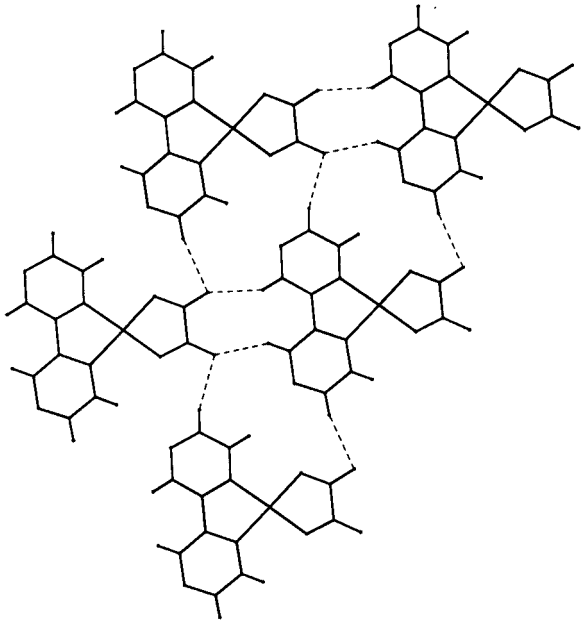


Figure 4. Complex units [Cu(bpz)(ox)] in **3** connected into layers through C−H···O contacts

Table 3. Selected bond lengths (Å) and angles (°) for $[Cu(bpz)(ox)]_n$ (**3**)[a]

| | | | |
|---|---|---|---|
| Cu(1)−O(2) | 1.9252(14) | Cu(1)−N(2) | 1.9869(16) |
| Cu(1)−O(1) | 1.9258(15) | Cu(1)−O(3b) | 2.6170(18) |
| Cu(1)−N(1) | 1.9837(17) | Cu(1)−O(1a) | 2.7518(17) |
| O(2)−Cu(1)−O(1) | 85.76(6) | N(1)−Cu(1)−O(3b) | 87.50(6) |
| O(2)−Cu(1)−N(1) | 96.37(6) | N(2)−Cu(1)−O(3b) | 85.73(6) |
| O(1)−Cu(1)−N(1) | 173.60(7) | O(2)−Cu(1)−O(1a) | 99.73(6) |
| O(2)−Cu(1)−N(2) | 173.99(7) | O(1)−Cu(1)−O(1a) | 83.69(6) |
| O(1)−Cu(1)−N(2) | 96.52(6) | N(1)−Cu(1)−O(1a) | 90.00(6) |
| N(1)−Cu(1)−N(2) | 81.96(7) | N(2)−Cu(1)−O(1a) | 86.07(6) |
| O(2)−Cu(1)−O(3b) | 88.43(6) | O(3b)−Cu(1)−O(1a) | 171.69(4) |
| O(1)−Cu(1)−O(3b) | 98.61(6) | | |
| O(1)−C(9) | 1.291(2) | O(4)−C(9) | 1.215(2) |
| O(2)−C(10) | 1.280(2) | C(9)−C(10) | 1.556(3) |
| O(3)−C(10) | 1.224(2) | | |
| C(9)−O(1)−Cu(1) | 111.67(13) | O(4)−C(9)−C(10) | 120.10(19) |
| C(9)−O(1)−Cu(1a) | 106.77(13) | O(1)−C(9)−C(10) | 114.49(17) |
| Cu(1)−O(1)−Cu(1a) | 96.31(6) | O(3)−C(10)−O(2) | 125.57(19) |
| C(10)−O(2)−Cu(1) | 111.88(12) | O(3)−C(10)−C(9) | 120.05(18) |
| C(10)−O(3)−Cu(1b) | 102.29(13) | O(2)−C(10)−C(9) | 114.38(17) |
| O(4)−C(9)−O(1) | 125.36(19) | | |
| N(1)−C(1) | 1.336(3) | N(4)−C(6) | 1.339(3) |
| N(1)−C(4) | 1.341(3) | C(1)−C(2) | 1.338(3) |
| N(2)−C(8) | 1.338(3) | C(3)−C(4) | 1.387(3) |
| N(2)−C(5) | 1.342(2) | C(4)−C(5) | 1.479(3) |
| N(3)−C(2) | 1.333(3) | C(5)−C(6) | 1.386(3) |
| N(3)−C(3) | 1.339(3) | C(7)−C(8) | 1.385(3) |
| N(4)−C(7) | 1.333(3) | | |
| C(1)−N(1)−C(4) | 118.78(18) | N(3)−C(3)−C(4) | 122.3(2) |
| C(1)−N(1)−Cu(1) | 127.01(15) | N(1)−C(4)−C(3) | 120.01(19) |
| C(4)−N(1)−Cu(1) | 114.20(13) | N(1)−C(4)−C(5) | 114.92(17) |
| C(8)−N(2)−C(5) | 118.25(17) | C(3)−C(4)−C(5) | 125.06(18) |
| C(8)−N(2)−C(1) | 127.49(14) | N(2)−C(5)−C(6) | 120.31(19) |
| C(5)−N(2)−Cu(1) | 114.24(13) | N(2)−C(5)−C(4) | 114.64(17) |
| C(2)−N(3)−C(3) | 116.4(2) | C(6)−C(5)−C(4) | 125.05(18) |
| C(7)−N(4)−C(6) | 116.5(2) | N(4)−C(6)−C(5) | 122.1(2) |
| N(1)−C(1)−C(2) | 119.8(2) | N(4)−C(7)−C(8) | 122.5(2) |
| N(3)−C(2)−C(1) | 122.7(2) | N(2)−C(8)−C(7) | 120.3(2) |

| D−H···A | D···A (Å) | H···A (Å) | D−H···A (°) |
|---|---|---|---|
| C(3)−H(3)···O(3c) | 3.192(3) | 2.39 | 144 |
| C(7)−H(7)···O(3d) | 3.370(3) | 2.48 | 160 |
| C(6)−H(6)···O(4c) | 3.077(3) | 2.25 | 148 |
| C(62)−H(2)···O(4e) | 3.247(3) | 2.35 | 162 |

[a] Symmetry operations used to generate equivalent atoms: (a) $1-x$, $-y$, $-z$; (b) $-x$, $-y$, $-z$; (c) $1+x$, $1+y$, $1+z$; (d) $1+x$, $1+y$, $z$; (e) $x$, $y$, $1+z$.

The overlap between parallel oxalate groups across the Cu(1)···O(3b)/Cu(1b)···O(3) bridge is associated with π-π stacking, with an interplanar spacing of 2.88 Å. The other pair of axial bonds [Cu(1)···O(1a)/Cu(1a)···O(1)] leads to overlap between oxalate and bpz groups, the distance from the oxalate plane to the overlapping bpz atoms ranging from 2.90 to 3.37 Å. The shortest intermetallic distance in the crystal, 3.5279(6) Å, is found between copper atoms linked by the latter type of oxalate bridge [Cu(1)···Cu(1a)]. The intermetallic distance across the Cu(1)−O(3b)/Cu(1b)−O(3) bridge is 4.8952(9) Å. The chains in the crystal are linked through C−H···O interactions, forming parallel layers (Figure 4, Figure S3 and Table 3).

To the best of our knowledge the only copper(II) bpz complex previously characterized by X-ray crystallography is $[Cu(bpz)(H_2O)(C_5O_5)]$ ($C_5O_5$ is the dianion of croconic acid).[18] In this compound an axially bound water molecule precludes a chain formation analogous to that found in **3**;

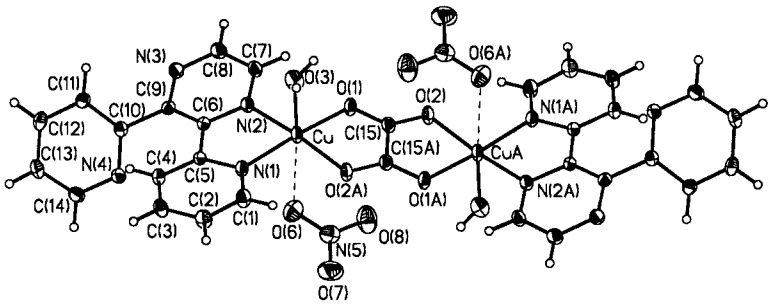



Figure 5. The complex unit $[Cu_2(dpp)_2(H_2O)_2((NO_3)_2(ox)]\cdot 4H_2O$ (**4**), showing the atomic numbering scheme; thermal ellipsoids are plotted at the 30% probability level; symmetry operations: (a) $1 - x$, $1 - y$, $1 - z$

instead the complex units are connected pairwise through weak Cu···O(croconate) interactions. The two pyrazine rings in **3** are practically coplanar (dihedral angle 3.3°), as was the case in the croconato compound. The bond lengths and angles involving bpz are similar in the two bpz-containing copper(II) compounds. Structures of a number of bpz complexes with $Ag^{I}$,[19] $Fe^{II}$,[20] $Co^{II}$,[21] $Ru^{II}$ and $Ru^{I}$,[22] $Pd^{II}$ and $Pt^{II}$ [23] have been reported. In several of these polynuclear complexes the simultaneous occurrence of the chelating and monodentate binding modes for this ligand[19,23] imposes a twist between the two pyrazine ligands.

### $[Cu_2(dpp)_2(H_2O)_2(NO_3)_2(ox)]\cdot 4H_2O$ (4)

The structure of **4** is built of centrosymmetric oxalato-bridged dinuclear $[Cu_2(dpp)_2(H_2O)_2(NO_3)_2(ox)]$ units (Figure 5) and water of hydration. The copper coordination may be described as elongated octahedral of the 4+1+1′ type, where two oxalate oxygen atoms and two dpp nitrogen atoms occupy the equatorial positions [1.982(2) and 1.990(2) Å for Cu−O and 1.960(2) and 1.981(2) Å for Cu−N]; a water molecule coordinates in one axial position [2.238(2) Å for $Cu-O_w$] and a semicoordinated nitrate oxygen atom completes the coordination sphere [2.750(3) Å for Cu−O]. The equatorial plane of copper is essentially planar [maximum atomic deviation 0.013 Å] and the copper atom is displaced by 0.160 Å toward the axial water molecule. The bis-bidentate bridging oxalate group is planar and makes a dihedral angle of 7.3° with the mean copper equatorial plane. The dihedral angles between the pyrazine ring and the coordinated and uncoordinated pyridyl rings are 13.0° and 39.4°, respectively. The plane of the nitrate makes dihedral angles of 15.3° and 19.4° with the oxalate group and the equatorial plane, respectively, the average distances between the individual nitrate atoms and the oxalate and equatorial planes being 3.01 and 2.96 Å, respectively. The intramolecular copper···copper distance across the oxalate bridge is 5.171(1) Å.

The packing of the dinuclear units in the crystal results in partial π-π overlap between the pyrazine ring and pyridyl rings of two neighbouring molecules, the distances from the pyrazine plane to the overlapping pyridyl atoms being in the range 3.29−3.63 Å (Figure S4). The molecules are connected by hydrogen bonds involving water, oxalate and nitrate (Table 4 and Figure S4). The shortest intermolecular metal···metal distance occurs between atoms displaced by a unit translation along the *b*-axis (7.2598 Å). The corresponding molecules are connected by hydrogen bonds between coordinated water and nitrate.

The oxalate shows the typical features of bis-bidentate bonding, with the four Cu−O bonds being of the same length [1.254(3)/1.248(3) Å], intermediate between the bond lengths found in bidentate oxalate. The dpp bond lengths and angles compare well with those of compound **2** and with previous findings.[16] The Cu−N(pyrazine) bond [1.981(2) Å] is slightly longer than the Cu−N(pyridyl) bond [1.960(2) Å], but they are still similar, in contrast to the observation in **1** where the pyrazine ring is part of the quinoxaline moiety and steric effects probably tend to lengthen the bond to pyrazine.

### $[Cu_2(bpz)_2(H_2O)_2Cl_2(ox)][Cu(bpz)(H_2O)_2(ox)]\cdot 2H_2O$ (5)

Two types of neutral complex units have cocrystallized in this compound: dinuclear $[Cu_2(bpz)_2(H_2O)_2Cl_2(ox)]$ and mononuclear $[Cu(bpz)(H_2O)_2(ox)]$ (Figure 6). The oxalate bridges the metal atoms in the bis-bidentate mode in the dinuclear unit whereas it acts as a bidentate ligand in the mononuclear one. A corresponding situation with coexistence of two analogous complex units in the same crystal was observed by some of us several years ago in copper(II) complexes of formula $[Cu_2(bipy)_2(H_2O)_2(ox)]X_n\cdot[Cu(bipy)(ox)]$ [X = $NO_3^-$, $BF_4^-$, $ClO_4^-$ ($n$ = 2) and $SO_4^{2-}$ ($n$ = 1)] where the bidentate bipy ligand was used instead of bpz.[1d,1i,10b] Each copper atom in the dinuclear unit of **5** has an elongated octahedral coordination sphere (4+1+1′ coordination) with two oxalate oxygen atoms [1.956(6) to 1.987(6) Å for Cu−O] and two bpz nitrogen atoms [1.988(7) to 2.009(7) Å for Cu−N] in the equatorial plane and a water molecule [2.509(7) and 2.514(7) Å for $Cu-O_w$] and a chlorine atom [2.629(3) and 2.649(3) Å for Cu−Cl] in the axial positions. The equatorial plane of each copper atom has a small tetrahedral distortion (maximum atomic deviations from the mean plane of 0.053 and 0.047 Å, respectively), and the copper atoms are displaced by 0.103 and 0.089 Å from this plane toward the axial chlorine atom. The dihedral angle between the bridging oxalate and either of the equatorial planes is 4.9°. The copper···copper distance across the bridging oxalate in the dinuclear unit is 5.1345(16) Å. The copper coordination geometry in the

Table 4. Selected bond lengths (Å) and angles (°) for $[Cu_2(dpp)_2(H_2O)_2((NO_3)_2(ox)]\cdot 4H_2O$ (**4**)[a]

| | | | |
|---|---|---|---|
| Cu−N(1) | 1.960 (2) | Cu−O(2a) | 1.990(16) |
| Cu−N(2) | 1.981(2) | Cu−O(3) | 2.238(2) |
| Cu−O(1) | 1.982(2) | Cu−O(6) | 2.750(3) |
| N(1)−Cu−N(2) | 85.76(6) | O(1)−Cu−O(3) | 96.24(8) |
| N(1)−Cu−O(1) | 169.51(8) | O(2a)−Cu−O(3) | 93.87(8) |
| N(2)−Cu−O(1) | 95.02(7) | N(1)−Cu−O(6) | 77.92(8) |
| N(1)−Cu−O(2a) | 97.85(7) | N(2)−Cu−O(6) | 88.80(7) |
| N(2)−Cu−O(2a) | 171.53(8) | O(1)−Cu−O(6) | 92.26(8) |
| O(1)−Cu−O(2a) | 84.39(6) | O(2a)−Cu−O(6) | 82.78(7) |
| N(1)−Cu−O(3) | 93.84(8) | O(3)−Cu−O(6) | 170.53(7) |
| N(2)−Cu−O(3) | 94.60(8) | | |
| O(1)−C(15) | 1.254(3) | C(15)−C(15a) | 1.532(5) |
| O(2)−C(15) | 1.248(3) | | |
| C(15)−O(1)−Cu | 110.93(14) | O(2)−C(15)−C(15a) | 117.2(3) |
| C(15)−O(2)−Cu(a) | 110.65(14) | O(1)−C(15)−C(15a) | 116.8(3) |
| O(2)−C(15)−O(1) | 126.0(2) | | |
| N(1)−C(1) | 1.331(3) | C(3)−C(4) | 1.387(3) |
| N(1)−C(5) | 1.356(3) | C(4)−C(5) | 1.381(3) |
| N(2)−C(7) | 1.328(3) | C(5)−C(6) | 1.494(3) |
| N(2)−C(6) | 1.358(39 | C(6)−C(9) | 1.405(3) |
| N(3)−C(8) | 1.326(3) | C(7)−C(8) | 1.374(3) |
| N(3)−C(9) | 1.348(3) | C(9)−C(10) | 1.496(3) |
| N(4)−C(10) | 1.340(3) | C(10)−C(11) | 1.386(3) |
| N(4)−C(14) | 1.341(3) | C(11)−C(12) | 1.385(3) |
| C(1)−C(2) | 1.375(4) | C(12)−C(13) | 1.375(4) |
| C(2)−C(3) | 1.373(3) | C(13)−C(14) | 1.374(4) |
| N(5)−O(6)−Cu | 109.7(2) | N(2)−C(6)−C(9) | 118.2(2) |
| C(1)−N(1)−C(5) | 119.8(2) | N(2)−C(6)−C(5) | 112.7(2) |
| C(1)−N(1)−Cu | 124.0(2) | C(9)−C(6)−C(5) | 129.0(2) |
| C(5)−N(1)−Cu | 116.13(15) | N(2)−C(7)−C(8) | 120.2(2) |
| C(7)−N(2)−C(6) | 120.2(2) | N(3)−C(8)−C(7) | 121.4(2) |
| C(7)−N(2)−Cu | 124.2(2) | N(3)−C(9)−C(6) | 120.4(2) |
| C(6)−N(2)−Cu | 115.56(14) | N(3)−C(9)−C(10) | 112.3(2) |
| C(8)−N(3)−C(9) | 118.9(2) | C(6)−C(9)−C(10) | 127.2(2) |
| C(10)−N(4)−C(14) | 116.5(2) | N(4)−C(10)−C(11) | 123.2(2) |
| N(1)−C(1)−C(2) | 122.6(2) | N(4)−C(10)−C(9) | 117.0(2) |
| C(3)−C(2)−C(1) | 118.3(2) | C(11)−C(10)−C(9) | 119.6(2) |
| C(2)−C(3)−C(4) | 119.7(2) | C(12)−C(11)−C(10) | 118.8(2) |
| C(5)−C(4)−C(3) | 119.4(2) | C(13)−C(12)−C(11) | 118.7(2) |
| N(1)−C(5)−C(4) | 120.1(2) | C(14)−C(13)−C(12) | 118.7(2) |
| N(1)−C(5)−C(6) | 113.6(2) | N(4)−C(14)−C(13) | 124.1(2) |
| C(4)−C(5)−C(6) | 126.2(2) | | |
| O(6)−N(5) | 1.238(3) | O(8)−N(5) | 1.247(3) |
| O(7)−N(5) | 1.224(3) | | |
| O(7)−N(5)−O(6) | 121.0(3) | O(6)−N(5)−O(8) | 119.4(3) |
| O7)−N(5)−O(8) | 119.6(3) | Cu−O(6)−N(5) | 109.67(18) |

| D−H···A[b] | D···A (Å) | H···A (Å) | D−H···A (°) |
|---|---|---|---|
| O(3)−H(31)···O(5a) | 2.830(3) | 2.10 | 156 |
| O(3)−H(32)···O(8b) | 2.819(3) | 2.07 | 169 |
| O(4)−H(41)···O(1) | 3.032(3) | 2.35 | 163 |
| O(4)−H(42)···O(5c) | 2.798(4) | 1.94 | 145 |
| O(5)−H(51)···O(7)* | 2.981(4) | 2.08 | 167 |
| O(5)−H(51)···O(8)* | 2.967(4) | 2.26 | 134 |
| O(5)−H(52)···O(4d) | 2.813(4) | 1.94 | 144 |

[a] Symmetry transformations used to generate equivalent atoms: (a) $1-x, 1-y, 1-z$; (b) $x, y-1, z$; (c) $1-x, 2-y, 1-z$; (d) $1+x, y, z$. [b] Bifurcated hydrogen bond.

mononuclear unit is also elongated octahedral. The equatorial bonds between copper and oxalate oxygen atoms are somewhat shorter [1.928(6) and 1.937(6) Å] than those found in the dinuclear compound, while the Cu−N bonds are of similar lengths [1.992(7) and 2.013(7) Å]. Both of the axial ligands are water molecules [2.506(7) and 2.541(7) Å for $Cu-O_w$]. The copper equatorial plane is close to planar (maximum atomic deviation 0.015 Å). It is essentially coplanar with oxalate (dihedral angle 1.4°) and makes an angle of 8.7° with the bpz best plane.

The standard deviations in the bond lengths and angles of compound **5** are somewhat higher than in **1**−**4**, but the typical feature of two long C−O oxalate bonds (for oxygen coordinated to copper) and two shorter bonds involving non-coordinated oxygen is clearly seen in the mononuclear unit, while in the dinuclear unit all the C−O bonds are equal within the limits of errors. In the dinuclear unit the two pyrazine rings within each bpz moiety are practically coplanar (dihedral angles 2.8 and 3.1°), as was found in **3** and the $[Cu(bpz)(H_2O)(C_5O_5)]$ complexes.[18] In the mononuclear unit of **5** the bpz ligand is slightly more twisted, the dihedral angle between the two pyrazine rings being 12.1°.

In the crystal the molecules are linked through hydrogen bonds (see Table 5) and partial π-π overlap, resulting in an arrangement of wave-type layers (Figure S5). The most pronounced π-π interaction appears to be between the bpz and oxalate groups of neighbouring mononuclear units, the average distance from oxalate atoms to bpz plane being 3.22 Å.

## IR Spectroscopy

The IR spectra of **1**−**5** have in common the occurrence of a strong and broad absorption centred at about 3420 $cm^{-1}$ which is due to the OH stretching of both coordinated and crystallization water molecules participating in hydrogen bonds.[24] The C−H stretching vibrations of dpp in **2** and **4** (triplet between 3200 and 3060 $cm^{-1}$) and bpz in **3** and **5** (quadruplet between 3100 and 2925 $cm^{-1}$) are also observed in the high-frequency region. In the case of complex **1**, the C−H stretching vibrations of dpq are obscured by the strong and broad OH absorption of the water molecules. The characteristic bands of bidentate (**1**, **2** and **5**) and bridging (**3**−**5**) oxalate are also observed in the IR spectra of this series:[1i,1o,1p,18,25,26] $\nu_{as}$(CO) vibration at 1708, 1650 and 1680 $cm^{-1}$ (**1**), 1705, 1685 and 1660 $cm^{-1}$ (**2**), 1712, 1680 and 1650 $cm^{-1}$ (**3**), 1640 $cm^{-1}$ (**4**) and 1710 sh, 1665 and 1640 $cm^{-1}$ (**5**); $\nu_s$(CO) stretching at 1411, 1357 and 1268 $cm^{-1}$ (**1**), 1395, 1295 and 1255 $cm^{-1}$ (**2**), 1406 and 1245 $cm^{-1}$ (**3**), 1360 and 1310 $cm^{-1}$ (**4**) and 1410, 1345, 1310 and 1275 $cm^{-1}$ (**5**); δ(OCO) vibration at 790 (**1**), 792 (**2**), 789 (**3**), 790 (**4**) and 794 $cm^{-1}$ (**5**). Finally, the bands observed at 1380, 1320 and 1080 $cm^{-1}$ in the IR spectrum of **4** suggest the occurrence of monodentate coordination of the nitrate ion.[27]

## Magnetic Properties

Compounds **3**−**5** were magnetically characterised by following the thermal variation of the magnetic susceptibility ($\chi_M$). The magnetic properties of compounds **1** and **2** were not investigated because they are mononuclear.

The temperature dependence of the $\chi_M T$ product for **3** is shown in Figure 7. At room temperature, $\chi_M T$ is equal to 0.41 $cm^3\cdot mol^{-1}\cdot K$, a value which is as expected for a magnetically isolated spin doublet. Upon cooling, $\chi_M T$ smoothly decreases to reach a value of about 0.26 $cm^3\cdot mol^{-1}\cdot K$ at 1.9 K. The shape of this plot is indicative of a weak antiferromagnetic interaction. In agreement with

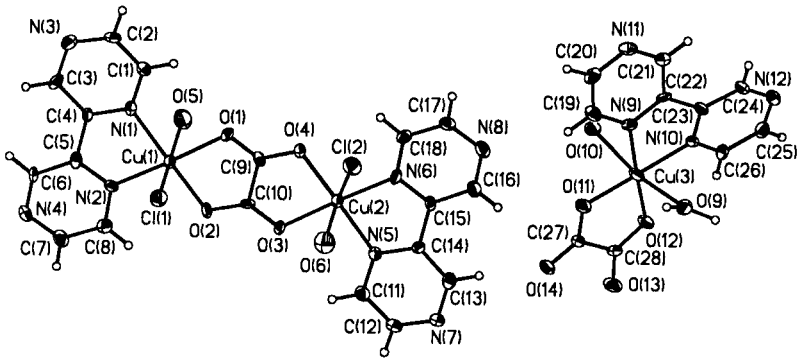



Figure 6. The dinuclear and mononuclear building blocks in $[Cu_2(bpz)_2(H_2O)_2Cl_2(ox)][Cu(bpz)(H_2O)_2(ox)]\cdot 2H_2O$ (**5**) showing the atom numbering scheme; thermal ellipsoids are plotted at the 30% probability level

the alternating chain structure of **3**, we analysed its magnetic data by the alternating-chain spin-exchange model through the Hamiltonian $\hat{H} = -J\Sigma(\hat{S}_{2i} \cdot \hat{S}_{2i-1} + \alpha\hat{S}_{2i} \cdot \hat{S}_{2i+1})$ where $J$ and $\alpha J$ are the alternating exchange-coupling parameters. The best-fit parameters are: $J = -1.44$ cm$^{-1}$, $\alpha J = -0.69$ cm$^{-1}$, $g = 2.10$ and $R = 1.4 \times 10^{-6}$; $R$ is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\Sigma_i[(\chi_M T)_{obs}(i)]^2$. The calculated curve reproduces the experimental data very well. The weak intrachain magnetic interactions in **3** are as expected taking into account the out-of-plane exchange coupling involved. In fact, the unpaired electron on each copper(II) ion in this compound is defined by a $d_{x^2-y^2}$-type magnetic orbital (the $x$ and $y$ axes corresponding roughly to the copper−nitrogen bonds) that is mainly centred on the metal atom. The interchain exchange pathway involves axially coordinated oxalate oxygen atoms [2.75 and 2.62 Å for Cu(1)−O(1a) and Cu(1)−O(3b), respectively] whose spin density must be very weak. Consequently, simple symmetry considerations show that the overlap between the planar magnetic orbitals through the out-of-plane exchange pathway has to be very small and a weak magnetic interaction (either antiferro- or ferromagnetic depending on structural parameters such as the angle at the atom of the bridge and value of the axial bond) is expected,[29] as observed. Looking at the different intrachain out-of-plane exchange pathways occurring in **3**, [Cu(1)O(1)O(1a)Cu(1a) and Cu(1)O(2)-C(10)O(3)O(3b)C(10b)O(2b)Cu(1b)], most likely the strongest antiferromagnetic interaction ($J = -1.44$ cm$^{-1}$) corresponds to the shorter pathway (double oxalate−oxygen bridge) whereas the weakest one ($\alpha J = -0.69$ cm$^{-1}$) is ascribed to the longer pathway. Concerning the significance of these coupling values, it should be noted that: (i) weak antiferromagnetic interactions between copper(II) ions through double oxalate−oxygen bridge were observed in the complexes $H_2Im[Cu(ox)_2]$ (Him = imidazole, $J = -1.09$ cm$^{-1}$)[2e] and $Na_2[Cu(ox)_2]\cdot 2H_2O$ ($J = -1.2$ cm$^{-1}$),[2b] and (ii) either weak antiferro- or ferromagnetic interactions were reported for the copper(II) complexes $M_2[Cu(ox)_2]\cdot 2H_2O$ [M = K$^+$ ($J = -0.7$ cm$^{-1}$) and $NH_4^+$ ($J = -0.6$ cm$^{-1}$)],[2a] $[Cu(pyim)(H_2O)(ox)]\cdot 2H_2O$ [pyim = 2-(2-pyridyl)imidazole, $J = +0.04$ cm$^{-1}$][18] and $[Cu(H_2bim)(H_2O)(ox)]\cdot H_2O$ [$H_2$bim = 2,2′-biimidazole, $J = -0.08$][18] where the longer out-of-plane exchange pathway occurs.

The temperature dependence of $\chi_M$ for **4** [$\chi_M$ is the magnetic susceptibility per two copper(II) ions] is shown in Figure 8. The thermal dependence of the $\chi_M T$ product is shown in the inset of this figure. At room temperature, $\chi_M T$ is equal to 0.45 cm$^3$·mol$^{-1}$·K, a value which is well below that expected for two magnetically isolated spin doublets [0.75 cm$^3$·mol$^{-1}$·K for $g = 2.0$]. This value strongly decreases when cooling and it vanishes at low temperatures. The susceptibility plot exhibits a maximum at 260 K. These features are characteristic of a strong antiferromagnetic interaction between the two copper(II) ions in **4**. The experimental data closely follow Equation (1)

$$\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-J/kT)]^{-1} + \text{tip} \quad (1)$$

which is the Bleaney−Bowers expression for a coupled dinuclear copper(II) complex, the Hamiltonian being $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$. $N$, $g$ and β have their usual meanings and the tip is the temperature-independent paramagnetism for two copper(II) ions (120 cm$^3$·mol$^{-1}$). The best-fit parameters are: $J = -312$ cm$^{-1}$, $g = 2.09$ and $R = 1.9 \times 10^{-5}$ ($R$ is the agreement factor defined as $\Sigma_i[(\chi_M)_{obs}(i) - (\chi_M)_{calc}(i)]^2/\Sigma_i[(\chi_M)_{obs}(i)]^2$). The strong intramolecular antiferromagnetic interaction in **4** is as expected keeping in mind the effective σ in-plane overlap between the two $d_{x^2-y^2}$ magnetic orbitals on each copper(II) ion [the $x$ and $y$ axes being roughly defined by the Cu(1)−N(1) and Cu(1)−N(2) bonds].[1c,1i,1e,5] This remarkable efficiency of the oxalato bridge to mediate strong antiferromagnetic interactions in dinuclear copper(II) complexes through the σ in-plane exchange pathway is well-known and it is illustrated by the magneto-structural data listed in Table 6. The small structural distortions in this series account for the differences observed in the magnetic coupling values.

The thermal dependence of the $\chi_M T$ product [per two copper(II) ions] for **5** is shown in Figure 9. $\chi_M T$ decreases upon cooling, tends to a quasi plateau at temperatures below 80 K and further decreases at very low temperatures. Keeping in mind that the structure of compound **5** contains both an oxalato-bridged copper(II) dinuclear unit and a

Table 5. Selected bond lengths (Å) and angles (°) for $[Cu_2(bpz)_2(H_2O)_2Cl_2(ox)][Cu(bpz)(H_2O)_2(ox)]\cdot 2H_2O$ (**5**)[a]

| | | | |
|---|---|---|---|
| Cu(1)−O(2) | 1.956(6) | Cu(2)−N(6) | 1.998(8) |
| Cu(1)−O(1) | 1.980(6) | Cu(2)−O(6) | 2.509(7) |
| Cu(1)−N(2) | 1.994(7) | Cu(2)−Cl(2) | 2.649(3) |
| Cu(1)−N(1) | 2.009(7) | Cu(3)−O(11) | 1.928(6) |
| Cu(1)−O(5) | 2.514(7) | Cu(3)−O(12) | 1.937(6) |
| Cu(1)−Cl(1) | 2.629(3) | Cu(3)−N(10) | 1.992(7) |
| Cu(2)−O(3) | 1.984(6) | Cu(3)−N(9) | 2.013(7) |
| Cu(2)−O(4) | 1.987(6) | Cu(3)−O(9) | 2.506(7) |
| Cu(2)−N(5) | 1.988(7) | Cu(3)−O(10) | 2.541(7) |
| O(2)−Cu(1)−O(1) | 85.2(2) | N(5)−Cu(2)−O(6) | 82.5(3) |
| O(2)−Cu(1)−N(2) | 96.1(3) | N(6)−Cu(2)−O(6) | 92.1(3) |
| O(1)−Cu(1)−N(2) | 176.6(3) | O(3)−Cu(2)−Cl(2) | 92.2(2) |
| O(2)−Cu(1)−N(1) | 170.7(3) | O(4)−Cu(2)−Cl(2) | 96.4(2) |
| O(1)−Cu(1)−N(1) | 97.0(3) | N(5)−Cu(2)−Cl(2) | 91.3(2) |
| N(2)−Cu(1)−N(1) | 81.2(3) | N(6)−Cu(2)−Cl(2) | 90.2(2) |
| O(2)−Cu(1)−O(5) | 89.5(3) | O(6)−Cu(2)−Cl(2) | 173.1(2) |
| O(1)−Cu(1)−O(5) | 84.2(3) | O(11)−Cu(3)−O(12) | 86.5(2) |
| N(2)−Cu(1)−O(5) | 92.7(3) | O(11)−Cu(3)−N(10) | 176.9(3) |
| N(1)−Cu(1)−O(5) | 81.8(3) | O(12)−Cu(3)−N(10) | 95.8(3) |
| O(2)−Cu(1)−Cl(1) | 94.4(2) | O(11)−Cu(3)−N(9) | 95.6(3) |
| O(1)−Cu(1)−Cl(1) | 91.5(2) | O(12)−Cu(3)−N(9) | 177.9(3) |
| N(2)−Cu(1)−Cl(1) | 91.5(2) | N(10)−Cu(3)−N(9) | 82.1(3) |
| N(1)−Cu(1)−Cl(1) | 94.5(2) | O(11)−Cu(3)−O(9) | 95.6(3) |
| O(5)−Cu(1)−Cl(1) | 173.96(19) | O(12)−Cu(3)−O(9) | 96.6(3) |
| O(3)−Cu(2)−O(4) | 85.4(2) | N(10)−Cu(3)−O(9) | 82.2(3) |
| O(3)−Cu(2)−N(5) | 96.0(3) | N(9)−Cu(3)−O(9) | 83.0(3) |
| O(4)−Cu(2)−N(5) | 172.1(3) | O(11)−Cu(3)−O(10) | 90.1(3) |
| O(3)−Cu(2)−N(6) | 176.9(3) | O(12)−Cu(3)−O(10) | 91.7(3) |
| O(4)−Cu(2)−N(6) | 96.3(3) | N(10)−Cu(3)−O(10) | 91.8(3) |
| N(5)−Cu(2)−N(6) | 81.9(3) | N(9)−Cu(3)−O(10) | 170.2(2) |
| O(4)−Cu(2)−O(6) | 89.8(3) | | |
| O(1)−C(9) | 1.239(10) | O(12)−C(28) | 1.280(10) |
| O(2)−C(10) | 1.262(10) | O(13)−C(28) | 1.241(10) |
| O(3)−C(10) | 1.239(10) | O(14)−C(27) | 1.225(10) |
| O(4)−C(9) | 1.253(10) | C(9)−C(10) | 1.551(10) |
| O(11)−C(27) | 1.293(11) | C(27)−C(28) | 1.522(12) |
| C(9)−O(1)−Cu(1) | 110.6(6) | O(3)−C(10)−O(2) | 126.8(8) |
| C(10)−O(2)−Cu(1) | 111.4(5) | O(3)−C(10)−C(9) | 117.4(7) |
| C(10)−O(3)−Cu(2) | 110.2(6) | O(2)−C(10)−C(9) | 115.6(6) |
| C(9)−O(4)−Cu(2) | 109.8(6) | O(14)−C(27)−O(11) | 121.5(8) |
| C(27)−O(11)−Cu(3) | 110.3(5) | O(14)−C(27)−C(28) | 121.8(8) |
| C(28)−O(12)−Cu(3) | 111.3(6) | O(11)−C(27)−C(28) | 116.5(8) |
| O(1)−C(9)−O(4) | 125.7(8) | O(13)−C(28)−O(12) | 125.0(9) |
| O(1)−C(9)−C(10) | 117.2(7) | O(13)−C(28)−C(27) | 119.7(8) |
| O(4)−C(9)−C(10) | 117.1(7) | O(12)−C(28)−C(27) | 115.3(8) |
| N(1)−C(4) | 1.325(11) | N(11)−C(21) | 1.311(11) |
| N(1)−C(1) | 1.349(11) | N(11)−C(20) | 1.348(13) |
| N(2)−C(5) | 1.325(11) | N(12)−C(24) | 1.330(12) |
| N(2)−C(8) | 1.337(11) | N(12)−C(25) | 1.348(12) |
| N(3)−C(2) | 1.323(12) | C(1)−C(2) | 1.344(12) |
| N(3)−C(3) | 1.348(12) | C(3)−C(4) | 1.394(12) |
| N(4)−C(6) | 1.313(12) | C(4)−C(5) | 1.516(13) |
| N(4)−C(7) | 1.324(13) | C(5)−C(6) | 1.377(12) |
| N(5)−C(14) | 1.337(10) | C(7)−C(8) | 1.392(13) |
| N(5)−C(11) | 1.344(11) | C(11)−C(12) | 1.386(13) |
| N(6)−C(15) | 1.325(11) | C(13)−C(14) | 1.384(12) |
| N(6)−C(18) | 1.342(11) | C(14)−C(15) | 1.487(12) |
| N(7)−C(12) | 1.316(12) | C(15)−C(16) | 1.393(12) |
| N(7)−C(13) | 1.340(11) | C(17)−C(18) | 1.383(13) |
| N(8)−C(16) | 1.333(12) | C(19)−C(20) | 1.375(13) |
| N(8)−C(17) | 1.336(12) | C(21)−C(22) | 1.394(12) |
| N(9)−C(22) | 1.324(11) | C(22)−C(23) | 1.481(12) |
| N(9)−C(19) | 1.336(12) | C(23)−C(24) | 1.385(12) |
| N(10)−C(26) | 1.285(10) | C(25)−C(26) | 1.374(12) |
| N(10)−C(23) | 1.365(11) | | |
| C(4)−N(1)−C(1) | 118.2(8) | N(2)−C(5)−C(6) | 121.1(9) |
| C(4)−N(1)−Cu(1) | 114.5(6) | N(2)−C(5)−C(4) | 113.9(7) |
| C(1)−N(1)−Cu(1) | 127.2(6) | C(6)−C(5)−C(4) | 124.9(8) |
| C(5)−N(2)−C(8) | 118.2(8) | N(4)−C(6)−C(5) | 122.9(8) |
| C(5)−N(2)−Cu(1) | 115.3(6) | N(4)−C(7)−C(8) | 124.4(10) |
| C(8)−N(2)−C(1) | 126.3(6) | N(2)−C(8)−C(7) | 118.3(9) |
| C(2)−N(3)−C(3) | 116.3(8) | N(5)−C(11)−C(12) | 120.8(8) |
| C(6)−N(4)−C(7) | 115.2(8) | N(7)−C(12)−C(11) | 122.6(9) |
| C(14)−N(5)−C(11) | 117.5(7) | N(7)−C(13)−C(14) | 123.0(9) |
| C(14)−N(5)−C(2) | 113.7(6) | N(5)−C(14)−C(13) | 120.0(8) |
| C(11)−N(5)−Cu(2) | 128.7(6) | N(5)−C(14)−C(15) | 115.2(7) |
| C(15)−N(6)−C(18) | 117.9(8) | C(13)−C(14)−C(15) | 124.8(8) |
| C(15)−N(6)−Cu(2) | 114.0(6) | N(6)−C(15)−C(16) | 120.9(8) |
| C(18)−N(6)−Cu(2) | 128.0(6) | N(6)−C(15)−C(14) | 114.8(7) |
| C(12)−N(7)−C(13) | 116.0(8) | C(16)−C(15)−C(14) | 124.2(8) |
| C(16)−N(8)−C(17) | 117.2(8) | N(8)−C(16)−C(15) | 121.4(9) |
| C(22)−N(9)−C(19) | 117.7(7) | N(8)−C(17)−C(18) | 121.6(8) |
| C(22)−N(9)−Cu(3) | 113.7(6) | N(6)−C(18)−C(17) | 120.8(8) |
| C(19)−N(9)−Cu(3) | 128.2(6) | N(9)−C(19)−C(20) | 120.5(9) |
| C(26)−N(10)−C(23) | 119.3(8) | N(11)−C(20)−C(19) | 122.5(9) |
| C(26)−N(10)−Cu(3) | 127.3(6) | N(11)−C(21)−C(22) | 122.6(9) |
| C(23)−N(10)−Cu(3) | 112.5(5) | N(9)−C(22)−C(21) | 120.7(8) |
| C(21)−N(11)−C(20) | 115.9(8) | N(9)−C(22)−C(23) | 115.4(8) |
| C(24)−N(12)−C(25) | 115.7(8) | C(21)−C(22)−C(23) | 123.8(9) |
| C(2)−C(1)−N(1) | 119.2(8) | N(10)−C(23)−C(24) | 118.5(8) |
| N(3)−C(2)−C(1) | 124.9(9) | N(10)−C(23)−C(22) | 114.8(7) |
| N(3)−C(3)−C(4) | 120.0(9) | C(24)−C(23)−C(22) | 126.6(9) |
| N(1)−C(4)−C(3) | 121.4(8) | N(12)−C(24)−C(23) | 123.0(9) |
| N(1)−C(4)−C(5) | 114.6(7) | N(12)−C(25)−C(26) | 122.2(9) |
| C(3)−C(4)−C(5) | 124.0(8) | N(10)−C(26)−C(25) | 121.3(9) |

| D[b] | A | D···A (Å) |
|---|---|---|
| O(5) | Cl(1a) | 3.323(8) |
| O(6) | Cl(2b) | 3.379(8) |
| O(7) | Cl(1d) | 3.263(9) |
| O(8) | Cl(2) | 3.292(10) |
| O(5) | O(8) | 2.868(11) |
| O(6) | O(7c) | 2.828(12) |
| O(7) | O(4) | 3.032(10) |
| O(8) | O(2d) | 3.108(11) |
| O(9) | O(10b) | 2.783(9) |
| O(10) | O(14d) | 2.696(9) |
| O(9) | N(3e) | 2.924(10) |
| O(10) | N(7d) | 2.923(10) |

[a] Symmetry transformations used to generate equivalent atoms: (a) $1 + x, y, z$; (b) $-1 + x, y, z$; (c) $x, y, 1 + z$; (d) $x, y, -1 + z$; (e) $-1 + x, 0.5 + y, -z$. [b] Possible hydrogen bonds. D = donor; A = acceptor.

mononuclear one, this plot is interpreted as follows: the strong decrease of $\chi_M T$ in the high temperature range is due to a strong antiferromagnetic interaction within the dinuclear entity whereas the quasi plateau corresponds to the Curie law behaviour expected for the mononuclear copper(II) unit; the decrease of $\chi_M T$ in the very low temperature range is attributed to intermolecular magnetic interactions between the mononuclear copper(II) entities. Consequently, the magnetic data of **5** were analysed with Equation (2)

$$\chi_M = (2N\beta^2 g_d^2/kT)[3 + \exp(-J/kT)]^{-1} + [N\beta^2 g_m^2/k(T - \theta)] + \text{tip} \quad (2)$$

which is the sum of the Bleaney−Bowers equations for a coupled dinuclear copper(II) species, the Curie law for a mononuclear copper(II) unit (with a θ term accounting for the magnetic interaction between the mononuclear entities) and the temperature-independent paramagnetism [180 $cm^3 \cdot mol^{-1}$ for three copper(II) ions]. $J$ is the magnetic coupling through the oxalate bridge in the dinuclear complex, and $g_d$ and $g_m$ are the mean $g$ factors for the di- and mononuclear complexes, respectively. A least-squares fit of the experimental data of **5** with Equation (2) leads to the following set of parameters:

Table 6. Selected magneto-structural data for oxalato-bridged copper(II) complexes of the type $[(AA)Cu(\mu\text{-ox})Cu(AA)]X_n$ exhibiting the σ in-plane exchange pathway

| AA[a] | X | Donor set | Dihedral angle[b] | $h_{Cu}$[c] | $d_{Cu\cdots Cu}$[d] | $J$[e] | Ref. |
|---|---|---|---|---|---|---|---|
| phen | $NO_3$ | $O_2N_2/O$ | 16.9 | 0.27 | 5.158(1) | −330 | [1f] |
| bipy | $NO_3$ | $O_2N_2/O$ | 3.2 | 0.16 | 5.154(1) | −386 | [1d,1i] |
| bipy | $ClO_4$ | $O_2N_2/O$ | 12.0 | 0.18 | 5.150(1) | −376 | [1i] |
| bipy | BF4 | $O_2N_2/O$ | 10.4 | 0.16 | 5.144(1) | −378 | [1i] |
| dpa | $NO_3$ | $O_2N_2/O_2$ | 7.2 | 0.08 | 5.22 | −305 | [1p] |
| tmen | $ClO_4$ | $O_2N_2/O$ | 8.4 | 0.18 | 5.147/5.167 | −385.4 | [1c,1e] |
| deen | $ClO_4$ | $O_2N_2/O_2$ | 3.9 | [f] | [f] | −300 | [4d] |
| mpz | $PF_6$ | $O_2N_2/O$ | 13.9 | 0.24 | [f] | −402 | [1g] |
| mpz | $NO_3$ | $O_2N_2O_2$ | 2.1 | 0.06 | [f] | −312 | [1g] |
| mpz | $NO_3$ | $O_2N_2/O_2$ | [f] | 0.12 | 5.217 | −284 | [1h] |
| dpp (**4**) | $NO_3$ | $O_2N_2/O_2$ | 7.3 | 0.16 | 5.171(1) | −312 | this work |
| bpz (**5**) | Cl | $O_2N_2/OCl$ | 4.9 | 0.10/0.09 | 5.1345(16) | −345 | this work |

[a] Abbreviations: phen = 1,10-phenantholine; bipy = 2,2′-bipyridine; dpa = 2,2′-dipyridylamine; tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; deen = *N*,*N*-diethylethane-1,2-diamine; mpz = mepirizole; dpp = 2,3-bis(2-pyridyl)pyrazine; bpz = 2,2′-bipyrazine. [b] Dihedral angle (°) between the mean oxalate and equatorial planes. [c] Out-of-plane displacement of the copper atom (Å). [d] Metal-metal separation across the oxalate bridge (Å). [e] Magnetic coupling in $cm^{-1}$. [f] Not reported.

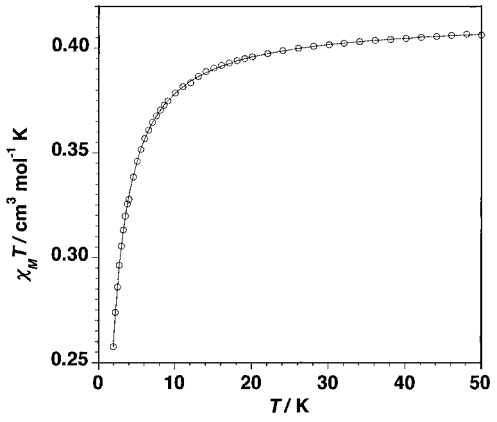



Figure 7. Thermal dependence of the $\chi_M T$ product for **3**: (o) experimental data; (−) best-fit curve (see text)

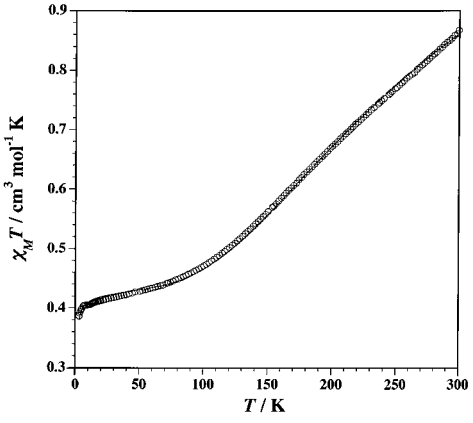



Figure 9. Thermal dependence of the $\chi_M T$ product for **5**: (o) experimental data; (−) best-fit curve from Equation (2) (see text)

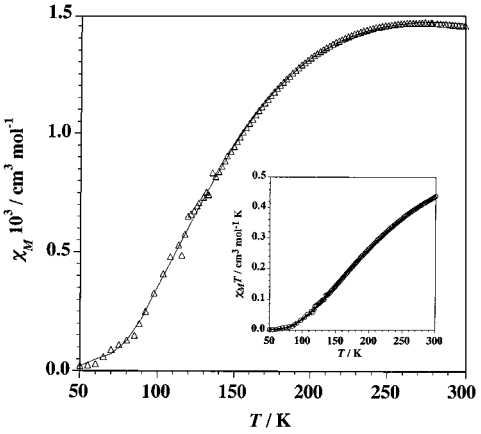



Figure 8. Thermal dependence of $\chi_M$ (Δ) and $\chi_M T$ (o) for **4**; the solid line is the best-fit curve through Equation (1) (see text)

$J = -345\ cm^{-1}$, $g_d = 2.05$, $g_m = 2.10$, $\theta = -0.3$ K and $R = 4.8 \times 10^{-5}$ ($R$ is the agreement factor defined as $\Sigma_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\Sigma_i[(\chi_M T)_{obs}(i)]^2$). The calculated curve reproduces very well the experimental data in the whole temperature range. The magnetic coupling in **5** compares well with that in complex **4** in agreement with the same σ in-plane exchange pathway that is involved in them. The slightly longer copper···copper separation across the bridging oxalate in **4** versus **5**, together with the somewhat larger dihedral angle between the oxalate and the mean equatorial plane in **4**, weaken somewhat the antiferromagnetic coupling in **4** as compared to that of **5** (see end of Table 6). The intermolecular interactions between the mononuclear units in the crystal of **5** (Figure S5 and Table 5) provide the exchange pathway for the weak antiferromagnetic coupling ($\theta = -0.3$ K) observed in the very low temperature range.

Finally, complex **5** provides an additional example of coexistence in the same crystal of the magnetic orbital [represented by the mononuclear copper(II) unit] and its combination through the oxalato bridge (dinuclear unit). Four examples of oxalate-containing copper(II) complexes with this special feature have previously been described, the blocking ligand being the parent bipy molecule.[1d,1i,10b]

## Conclusions

The use of oxalate with the blocking ligands dpq, dpp and bpz has led to the preparation of five new copper(II) complexes with terminal (**1**, **2** and **5**) and bridging (**3**−**5**) oxalate. Strong (**4** and **5**) and weak (**3**) antiferromagnetic interactions between the copper(II) ions across bridging oxalato are observed, in agreement with the σ in-plane (**4** and **5**) and out-of-plane (**3**) exchange pathways involved. This study illustrates once more the importance of a detailed structural knowledge when interpreting magnetic properties.

## Experimental Section

**Materials:** Copper(II) nitrate trihydrate, copper(II) chloride dihydrate, copper(II) triflate and potassium oxalate monohydrate were purchased from commercial sources and used as received. Cu(ox)·1/3$H_2O$ and the ligands dpp, dpq and bpz were prepared as reported in the literature.[6,30−32] Elemental analyses (C,H,N) were carried out by the Microanalytical Service of the Universidad Autónoma de Madrid.

**Compound 1:** dpq (0.106 g, 0.5 mmol) was added to 100 mL of an $H_2O$/EtOH (80:20, v/v) mixture containing $Cu(NO_3)_2·3H_2O$ (0.17 g, 0.5 mmol) and the resulting brown solution was gently refluxed for fifteen minutes. Then, $K_2ox·H_2O$ (0.092 g, 0.5 mmol) was added whilst stirring and the solution turned olive green in a few minutes. Dark green parallelepipeds of **1** suitable for X-ray diffraction were obtained by slow evaporation of the solvent at room temperature. Yield 75%. $C_{20}H_{24}CuN_4O_{10}$ (543.97): calcd. C 44.18, H 4.41, N 10.30; found C 43.96, H 4.35, N 10.21.

**Compound 2:** Cu(ox)·1/3$H_2O$ (g, 0.5 mmol) and dpp (g, 0.5 mmol) were suspended in 50 mL of an $H_2O$/EtOH (50:50 v/v) mixture and refluxed during half an hour under continuous stirring. The resulting blue solution was filtered and allowed to evaporate at room temperature. Single crystals of **2** were obtained as deep-blue parallelepipeds after a few days. Yield 85%. $C_{16}H_{14}CuN_4O_6$ (421.85): calcd. C 45.57, H 3.32, N 13.28; found C 45.36, H 3.25, N 13.19.

**Compound 3:** Solid bpz (0.030 g, 0.20 mmol) was added with stirring to an aqueous solution (20 mL) containing $Cu(CF_3SO_3)_2$ (0.072 g, 0.20 mmol). Then, $K_2ox·H_2O$ (0.018 g, 0.10 mmol) dissolved in a minimum amount of water (5 mL) was slowly added. X-ray quality crystals of **3** were grown as blue polyhedra from the resulting solution on standing at room temperature. Yield 70% (on the basis of oxalate). $C_{10}H_6CuN_4O_4$ (309.73): calcd. C 38.79, H 1.94, N 18.09; found C 38.50, H 1.88, N 17.96.

**Compound 4:** $Cu(NO_3)_2·3H_2O$ (0.032 g, 0.26 mmol) was dissolved in 5 mL of EtOH/$H_2O$ (1:1 mixture) and added to a solution of dpp (0.060 g, 0.26 mmol) in 15 mL of EtOH/$H_2O$. $K_2ox·H_2O$ (0.023 g, 0.13 mmol) (3:4 mixture) was then added to the resulting solution whilst stirring. After evaporation of the solvents at room temperature, green prisms of **4** suitable for X-ray diffraction appeared. Yield 70%. $C_{30}H_{32}Cu_2N_{10}O_{16}$ (915.74): calcd. C 39.35, H 3.52, N 15.30; found C 39.21, H 3.37, N 15.20.

**Compound 5:** Solid bpz (0.030 g, 0.20 mmol) was added with stirring to an aqueous solution (20 mL) containing $CuCl_2·2H_2O$ (0.034 g, 0.20 mmol). Then, $K_2ox·H_2O$ (0.018 g,0.10 mmol) dissolved in a minimum amount of water (5 mL) was slowly added with continuous stirring. X-ray quality crystals of **5** were grown as green polyhedra from the resulting solution on standing at room temperature. Yield 60% (on the basis of oxalate). $C_{28}H_{30}Cl_2Cu_3N_{12}O_{14}$ (1020.2): calcd. C 32.98, H 2.94, N 16.47; found C 32.79, H 2.83, N 16.38.

**Physical Measurements:** IR spectra of **1**−**5** (4000−400 $cm^{-1}$) were recorded on a Bruker IF S55 spectrophotometer with samples prepared as KBr pellets. Variable-temperature (2−290 K) magnetic susceptibility measurements on polycrystalline samples of **3**−**5** were carried out with a Quantum Design SQUID susceptometer using an applied magnetic field of 1000 G over the whole temperature range. The complex $(NH_4)_2Mn(SO_4)_2·6H_2O$ was used as a susceptibility standard. Diamagnetic corrections for the constituent atoms were estimated from Pascal's constants[33] as $-132 \times 10^{-6}$ (**3**), $-433 \times 10^{-6}$ (**4**) and $-604 \times 10^{-6}$ $cm^3·mol^{-1}$ (**5**). Corrections for the sample holder were also applied.

**Crystal Structure Determination:** Diffraction data for **1**, **2**, **3** and **5** were collected with a Bruker-AXS SMART 2 K CCD area detector diffractometer at 173 K (**1**, **2**) and 293 K (**3**, **5**). In the case of **4**, data were collected at 293 K with an Enraf-Nonius CAD-4 diffractometer. Crystal parameters and refinement results are listed in Table 7. Empirical absorption corrections were carried out using SADABS for compounds **1**, **2**, **3** and **5**,[34a] while a semiempirical correction based on psi-scans of six reflections was used for **4**.[34b] The structures were solved by direct methods and refined by full-matrix least-squares based on $F^2$, including all reflections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon were included at idealized positions, whereas those of water molecules were located in Fourier difference maps (the hydrogen atoms of only one of the water molecules were detectable in the difference map of compound **5**). All hydrogen atoms included in the structure factor calculation were refined according to the riding model. The two triclinic compounds (**1** and **3**) were both found to belong to the centrosymmetric space group. In the case of compound **3**, the structure was initially solved in the non-centrosymmetric space group $P1$, but conversion to $P\bar{1}$ was later done, as solution and refinement showed this to be the correct choice. For the two monoclinic compounds where the space groups were not determined uniquely by the systematic absences (**2** and **5**), the structure solutions and refinements confirmed the non-centrosymmetric choice ($P2_1$). Refinement of racemic twinning was performed for compound **5** yielding 0.38:0.62 as the fractional contributions of the twin components.

Data collection and data reduction for **1**, **2**, **3** and **5** were done with the SMART and SAINT programs,[35a,35b] whereas for **4** the CAD-Express and XCAD programs[35c,34b] were used. All other calculations were performed with SHELXS-86, SHELXL-93, SHELXS-97, SHELXL/PC and XP.[36]

CCDC-240026 to -240030 for **1**−**5**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

**Supporting Information** (see also footnote on the first page of this article): Figures of the crystal packing (Figures S1−S5) for complexes **1**−**5**.

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Table 7. Crystal data and structure refinement for complexes **1**−**5**

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{20}H_{24}CuN_4O_{10}$ | $C_{16}H_{14}CuN_4O_6$ | $C_{10}H_6CuN_4O_4$ | $C_{30}H_{32}Cu_2N_{10}O_8$ | $C_{28}H_{30}Cl_2Cu_3N_{12}O_{14}$ |
| Molecular mass | 543.97 | 421.85 | 309.73 | 915.74 | 1020.16 |
| Temperature (K) | 173 | 173 | 293 | 293 | 293 |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | triclinic | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P2_1$ | $P\bar{1}$ | $P2_1/c$ | $P2_1$ |
| $a$ (Å) | 9.2591(3) | 6.4964(2) | 7.1385(11) | 9.704(29 | 6.7920(14) |
| $b$ (Å) | 10.3134(4) | 11.0218(39 | 8.9032(13) | 7.2598(6) | 40.908(8) |
| $c$ (Å) | 12.6911(4) | 11.8647(3) | 9.4900(14) | 25.865(3) | 6.9587(14) |
| $\alpha$ (°) | 86.187(1) | | 108.092(3) | | |
| $\beta$ (°) | 74.485(19 | 102.5180(10) | 97.066(3) | 97.395(9) | 105.980(5) |
| $\gamma$ (°) | 83.804(1) | | 108.374(3) | | |
| $V$ (Å$^3$) | 1160.03(7) | 829.34(4) | 527.53(14) | 1807.0(4) | 1858.7(6) |
| Z | 2 | 2 | 2 | 2 | 2 |
| $\rho$ (Mg·m$^{-3}$) | 1.557 | 1.689 | 1.950 | 1.683 | 1.823 |
| $\mu$ (mm$^{-1}$) | 1.005 | 1.362 | 2.088 | 1.266 | 1.929 |
| Max. 2θ (°) | 56.0 | 56.5 | 64.1 | 49.9 | 50.1 |
| Refl. collected | 16730 | 6362 | 4945 | 3593 | 11317 |
| Independent refl. | 5602 [$R$(int) = 0.0436] | 3724 [$R$(int) = 0.0301] | 3304 [$R$(int) = 0.0198] | 3171 [$R$(int) = 0.0163] | 6112 [$R$(int) = 0.0636] |
| Refl. with $I > 2\sigma(I)$ | 4424 | 3585 | 2638 | 2677 | 4307 |
| Data/restraints/param. | 5602/0/316 | 3724/1/244 | 3304/0/172 | 3171/0/262 | 6112/1/533 |
| Goodness-of-fit on $F^2$ | 1.041 | 1.035 | 1.029 | 1.051 | 0.977 |
| $R$ [$I > 2\sigma(I)$] | 0.0365 | 0.0325 | 0.0331 | 0.0296 | 0.0571 |
| $R_w$ [$I > 2\sigma(I)$] | 0.0764 | 0.0860 | 0.0777 | 0.0672 | 0.1226 |
| Flack parameter | | 0.011(12) | | | |
| Twin comp. contributions | | | | | 0.38(2)/0.62(2) |


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