Ferromagnetic coupling in the malonato-bridged copper(II) chains $[Cu(Im)_2(mal)]_n$ and $[Cu(2\text{-}MeIm)_2(mal)]_n$ (H_2mal = malonic acid, Im = imidazole and 2-MeIm = 2-methylimidazole)

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Two new malonato-bridged copper(II) complexes of formula $[Cu(Im)_2(mal)]_n$ (**1**) and $[Cu(2\text{-}MeIm)_2(mal)]_n$ (**2**) (Im = imidazole, 2-MeIm = 2-methylimidazole and mal = malonate dianion) have been prepared and their structures solved by X-ray diffraction methods. The $[Cu(Im)_2(mal)]$ and $[Cu(2\text{-}MeIm)_2(mal)]$ neutral entities act as monodentate ligands towards the adjacent copper(II) units through one of the two carboxylate groups, the OCO bridge exhibiting an *anti-anti* conformation. The environment of each copper atom in **1** and **2** is distorted square pyramidal: two carboxylate oxygen atoms from a bidentate malonate and two nitrogen atoms from two imidazole (**1**) or 2-methylimidazole (**2**) ligands form the equatorial plane whereas the apical position is occupied by a carboxylate oxygen from the malonate group of the neighbouring complex unit. The intrachain copper-copper separation is 6.036(2) (**1**) and 6.099(2) Å (**2**). The magnetic properties of **1** and **2** have been investigated in the temperature range 1.9–290 K. Overall, ferromagnetic behaviour is observed in both cases and the intrachain magnetic coupling (J) between the copper(II) ions through the carboxylato group is found to be 1.64 (**1**) and 0.39 cm^{-1} (**2**) (the Hamiltonian being $H = -J\Sigma_i S_i \cdot S_{i+1}$).

The versatility of malonate (dianion of propanedioic acid, H_2mal) as a ligand can be illustrated by the variety of crystal structures of malonate-containing copper(II) complexes.[1–11] The adoption of bidentate (through the OCCCO fragment) and/or bridging (through the OCO unit) coordination modes makes this ligand very appropriate in designing mono-[2,3,6,9] and polynuclear species.[1,4,5–11] In addition, the observed ferro- and antiferromagnetic interactions between the copper(II) ions bridged by the carboxylate in the *anti-syn* and *anti-anti* conformations enhance the interest in this type of compounds.[10–16]

Focusing on the synthetic aspects of copper(II)-malonate chemistry, two strategies have been successfully used. In one of them, the homoleptic $[Cu(mal)_2]^{2-}$ complex is used as a ligand towards metal ions, allowing the isolation of homometallic dimers[4,10] and trimers,[10] as well as bimetallic one-[9] and two-dimensional compounds.[8] In the other one, the starting copper(II) precursor is a neutral heteroleptic species that contains only one malonate group and additional coligands (L). The coordination capability of the coligands, together with the possibility of the malonate carboxylate to act as a bridge, leads to a great variety of either mononuclear or extended systems. Thus, when L is benzylimidazole (bzIm) or 4,4′-bipyridine (4,4′-bpy), the one- and two-dimensional $[Cu(mal)(bzIm)(H_2O)]$[5] and $[Cu_2(mal)_2(4,4'\text{-}bpy)(H_2O)_2]\cdot H_2O$[7] compounds are obtained, respectively. Malonate exhibits the same bidentate and bridging coordination modes in both compounds, but the different coordination modes of the coligands involved, monodentate (bzIm) and bridging (4,4′-bpy), account for their different structures. The use of coligands such as the bidentate 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy) and *N*-methylethylenediamine (men), allowed the preparation of the mononuclear complexes $[Cu(phen)(mal)(H_2O]\cdot 1.5H_2O$[3] and $[Cu(bpy)(mal)(H_2O)]\cdot H_2O$[6] as well as the dinuclear species $[Cu(men)(mal)(H_2O)]_2$.[1] In all three compounds, the copper environment is distorted square pyramidal with the bidentate malonate and coligand groups in the equatorial positions and a water molecule (monomers) or an oxygen atom from a malonate carboxylate (dimer) in the apical position. A very recent report concerning the structure of the copper(II) chain $\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$ exemplifies the use of the mononuclear $[Cu(bpy)(mal)(H_2O)]$ unit as a ligand.[11] Intrachain ferro- (through the OCO carboxylate) and antiferromagnetic (through the OCCCO fragment) interactions were found in this compound.

In the context of our current research work exploring the second strategy, we prepared the chain compounds of formula $[Cu(Im)_2(mal)]_n$ (**1**) and $[Cu(2\text{-}MeIm)_2(mal)]_n$ (**2**) (Im = imidazole, 2-MeIm = 2-methylimidazole). Their synthesis, crystal structure determination and magnetic properties are presented here.

Results and discussion

Description of the structures

The structures of complexes **1** and **2** consist of regular zig-zag chains of $[Cu(Im)_2(mal)]$ (**1**) [Fig. 1(a)] and $[Cu(2\text{-}MeIm)_2\text{-}$

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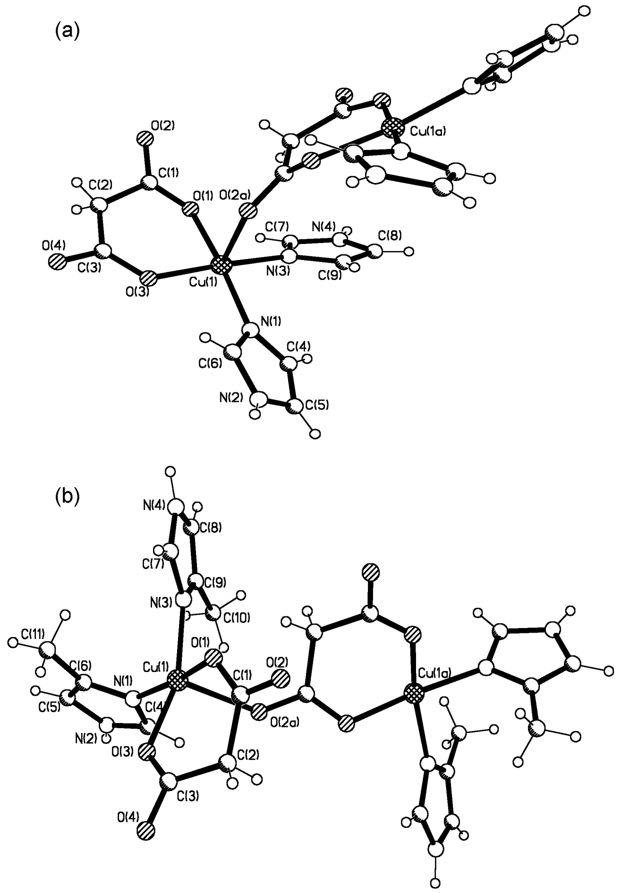


Fig. 1 Perspective view of the asymmetric unit of **1** (a) and **2** (b) with a symmetry-related unit and the atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

(mal)] (**2**) [Fig. 1(b)] units that are linked through one malonate carboxylate group exhibiting the *anti-anti* conformation. The chains run parallel to the *b* (**1**) (Fig. 2) and *a* (**2**) (Fig. 3) axes. The chains in **1** are interconnected through hydrogen bonds (Fig. 2) involving the uncoordinated imidazole nitrogen N(2) and malonate oxygen O(4c) atoms [2.683(4) Å for N(2)···O(4c); (c) = $-x+2,\ -y+2,\ -z$]. The chains in **2** are also linked by hydrogen bonds (Fig. 3) involving the uncoordinated nitrogen atom N(4) of a 2-methylimidazole group and the coordinated malonate oxygen O(2d) [3.185(7) Å for N(4)···O(2d); (d) = $-x-1/2,\ -y-1/2,\ -z+2$]. Additional intrachain C–H(Im or 2-MeIm)···O(mal) contacts contribute to the stabilization of the crystal structures of **1** and **2**. The Im (**1**) and 2-MeIm (**2**) ligands (Figs. 2 and 3) exhibit a parallel columnar arrangement, the inter-ring separation being 5.205(1) (**1**) and 5.405(1) Å (**2**).

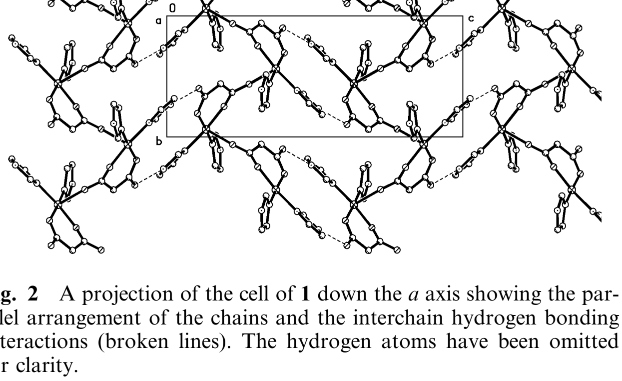


Fig. 2 A projection of the cell of **1** down the *a* axis showing the parallel arrangement of the chains and the interchain hydrogen bonding interactions (broken lines). The hydrogen atoms have been omitted for clarity.

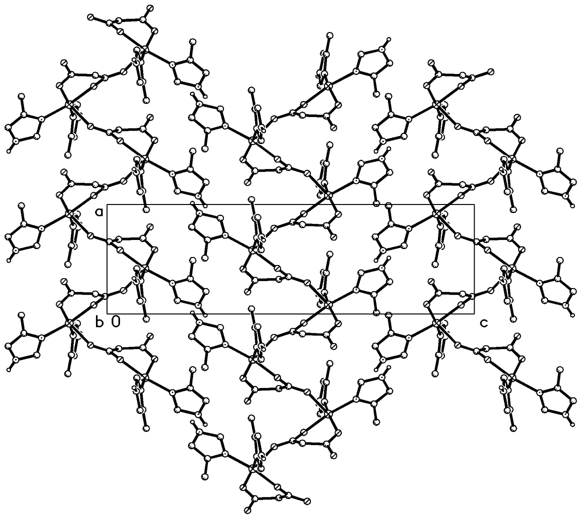


Fig. 3 A projection of the cell of **2** down the *b* axis showing the parallel arrangement of the chains and the columnar stacking of the 2-MeIm ligands.

Each copper(II) atom in **1** and **2** exhibits a distorted CuN_2O_3 square pyramidal geometry. The distortion is much smaller in the former compound as indicated by the calculated value of the τ factor,[17] which is 0.02 in **1** *vs.* 0.18 in **2** (the τ values for square pyramidal and trigonal bipyramidal metal environments are 0 and 1, respectively). Two carboxylate oxygen atoms [O(1) and O(3)] from the bidentate malonate ligand and two nitrogen atoms [N(1) and N(3)] from two monodentate imidazole (**1**) or 2-methylimidazole (**2**) groups build the basal plane, the mean value of the Cu–O bonds [1.947(2) Å (**1**) and 1.967(3) Å (**2**)] being somewhat shorter than that of the Cu–N ones [1.990(2) Å (**1**) and 2.008(4) Å (**2**)]. The average value of the copper to malonate bond distance lies within the range observed for other malonate-containing copper(II) complexes.[1–11] The Cu–N(Im) (**1**) and Cu–N(2-MeIm) (**2**) bond lengths agree with those reported for other copper(II) complexes with these ligands.[18,19] The apical position of the copper atom is occupied by a relatively strongly bound carboxylate oxygen from another unidentate malonate ligand both in **1** [2.394(2) Å for Cu(1)–O(2a); (a) = $3/2-x,\ 1/2+y,\ 1/2-z$] and in **2** [2.270(4) Å for Cu–O(2a); (a) = $x-1/2,\ 1/2-y,\ -z+2$]. The copper atom is shifted by 0.1134(4) (**1**) and 0.2434(5) Å (**2**) from the mean basal plane towards the apical position.

Each malonate group adopts simultaneously bidentate [through O(1) and O(3) atoms towards Cu(1)] and monodentate [through O(2) towards Cu(1b); (b) = $3/2-x,\ y-1/2,\ 1/2-z$ (**1**) and (b) = $1/2+x,\ 1/2-y,\ -z+2$ (**2**)] coordination modes. It exhibits an envelop conformation in which only the methylene group is significantly shifted from the chelate ring plane. The angles subtended at the copper atom by the chelating malonato group are 92.20(1)° (**1**) and 89.59(1)° (**2**). The average C–O bond distance and O–C–O bond angles are 1.249(3) (**1**) and 1.256(6) Å (**2**) and 123.05(2)° (**1**) and 122.55(5)° (**2**). The O(1)–C(1)–O(2) carboxylate bridge adopts an *anti-anti* conformation. The values of the dihedral angle between the equatorial plane at Cu(1) and that of O(1)C(1)O(2) are 20.87(1)° (**1**) and 22.96(4)° (**2**).

The two imidazole groups in **1** are practically planar, the largest deviation from the mean plane being 0.052(3) Å for C(7). The values of the dihedral angle between the equatorial plane at Cu(1) and the two imidazole mean planes are 28.20(1)° and

38.97(1)°. The intra-ring mean C–N [1.345(4) Å] and C–C [1.344(4) Å] bond lengths are as expected. The value of the dihedral angle between the mean planes of the two imidazole ligands is 52.31(1)°. As in **1**, the two imidazole rings in **2** are essentially planar, with atom-to-plane distances less than 0.012(7) Å and the methyl carbon atoms C(10) and C(11) being 0.05(8) and 0.06(9) Å, respectively, out of the plane. The values of the dihedral angles between the equatorial plane at Cu(1) and the two 2-MeIm mean planes are 82.4(1)° and 81.88(1)°. The intra-ring mean C–N [1.350(7) Å] and C–C [1.321(6) Å] bond lengths as well as the C(Im)–C(methyl) bond distance [mean value 1.488(8) Å] are as expected. The value of the dihedral angle between the mean planes of the two MeIm ligands is 74.88(2)°.

The intrachain copper-copper separations [6.036(2) (**1**) and 6.099(2) Å (**2**)] are significantly shorter than the shortest interchain copper-copper separation [7.791(2) (**1**) and 8.231(3) Å (**2**)].

Infrared spectra

In addition to several absorption bands observed at higher frequencies (3400–3000 cm^{-1}), which are characteristic of the Im and 2-MeIm groups, three strong peaks corresponding to the ν_{as}(OCO) vibration are observed at 1603, 1578 and 1543 cm^{-1} for **1** and at 1616, 1585 and 1562 cm^{-1} for **2**. The ν_s(OCO) stretching vibration is observed at 1438 and 1370 cm^{-1} for **1** and at 1440 and 1361 cm^{-1} for **2**. The fact that several absorptions bands occur for ν_{as} indicates a difference in the mode and the strength of binding of the carboxylate groups to the metal ion,[20] in agreement with the crystal structure. Only one peak is observed for ν_{as} at 1581 cm^{-1} for the complex [Cu(H$_2$O)$_6$][Cu(mal)$_2$(H$_2$O)] where the two malonate groups act as bidentate ligands towards one copper atom.[21] Taking into account that one of the carboxylato groups is not bridging in complexes **1** and **2**, the peaks at 1578 and 1585 cm^{-1} would correspond to these nonbridging carboxylates, whereas the remaining ones could be ascribed to the bridging carboxylates. The δ(OCO) absorptions are located at 749 and 730 for **1** and at 745 and 728 cm^{-1} for **2**.

Magnetic properties

The magnetic properties of **1** and **2** in the form of $\chi_M T$ *vs.* T [χ_M being the molar magnetic susceptibility per copper(II) ion] for compounds **1** and **2** are shown in Fig. 4. The values of $\chi_M T$ at room temperature are 0.41 and 0.42 cm^3 mol^{-1} K for **1** and **2**, respectively, values that are those expected for a magnetically isolated spin doublet. $\chi_M T$ continuously increases when cooling down and increases sharply below 30 K, reaching a value of 0.85 (**1**) and 0.55 cm^3 mol^{-1} K (**2**). The shape of this curves reveals the occurrence of significant ferromagnetic coupling between the copper(II) ions in **1** and **2**, the magnitude of the magnetic interaction being greater in the former compound. The shape of the magnetization curves at 2.0 K (see inset of Fig. 4) and the magnitude of the saturation value, which is nearly attained at the maximum of the magnetic field available, are in agreement with the occurrence of ferromagnetic coupling in **1** and **2**.

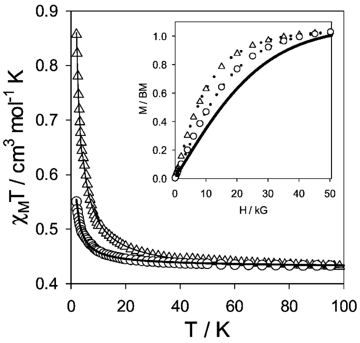


Fig. 4 Thermal dependence of the $\chi_M T$ product for complexes **1** (Δ) and **2** ($\bigcirc$); solid lines are the best fit from eqn. (1) (see text). The inset shows the magnetization curves at 2.0 K for **1** (Δ) and **2** ($\bigcirc$) (the dotted line is an eye-guide); the solid line represents the Brillouin function for a spin doublet.

As the structures of **1** and **2** consist of regular chains in which the copper(II) ions are bridged by the malonate carboxylate in the *anti-anti* conformation, we have analyzed their magnetic properties through the numerical expression proposed by Baker *et al.*[22] for a ferromagnetic copper(II) uniform chain:

$$\chi_M = (N\beta^2 g^2/4kT)(A/B)^{2/3} \tag{1}$$

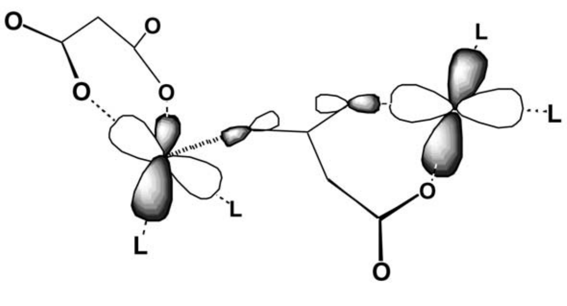
with

$$A = 1.0 + 5.7979916y + 16.902653y^2 + 29.376885y^3 + 29.832959y^4 + 14.036918y^5 \tag{2}$$

$$B = 1.0 + 2.7979916y + 7.0086780y^2 + 8.6538644y^3 + 4.5743114y^4 \tag{3}$$

and $y = J/2kT$. J is the intrachain magnetic coupling parameter and the other symbols have their usual meanings. The best fit obtained using a nonlinear regression analysis leads to $J = 1.64(1)$ cm^{-1}, $g = 2.12(1)$ and $R = 5.7 \times 10^{-5}$ for **1** and $J = 0.39(1)$ cm^{-1}, $g = 2.15(1)$ and $R = 1.5 \times 10^{-5}$ for **2**. R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{\text{obs}}(i) - (\chi_M T)_{\text{calc}}(i)]^2/\Sigma[(\chi_M T)_{\text{obs}}(i)]^2$.

In the light of these magneto-structural results for **1** and **2**, two facts warrant mention: (*i*) the nature of the intrachain magnetic coupling and (*ii*) the significantly larger magnetic coupling in **1**. As far as the first point is concerned, the ferromagnetic nature of the interaction can be explained since the CuOCOCu exchange pathway involves an equatorial position at one copper(II) ion and an axial position of the nearest neighbouring copper(II). This behaviour has been observed in other carboxylate-bridged copper(II) complexes.[9b,10,16e] The magnetic orbital on each copper(II) ion in **1** and **2** is defined by the four equatorial Cu–N and Cu–O bonds (see Scheme 1) and is thus mainly localized in the equatorial plane ($d_{x^2-y^2}$ type orbital). A low spin density is expected in the axial position because of some admixture of d_{z^2} character due to the trigonal distortion of the metal environment. The small overlap between the magnetic orbitals of adjacent copper(II) ions through the out-of-plane exchange pathway that connects the equatorial Cu(1)–O(1) bond with the axial Cu(1a)–O(2a) one [Cu(1)–O(1)–C(1)–O(2)–Cu(1a) skeleton] reduces the antiferromagnetic contribution, which is proportional to the square of the overlap between the magnetic orbitals in Kahn's orbital model.[23] In this model, the magnetic coupling for a copper(II) dimer (J) is the sum of two terms of opposite sign, one antiferro- (J_{AF}) and the other ferromagnetic (J_F). When



Scheme 1

the overlap is minimized the J_{AF} term is very small and the ferromagnetic term may become dominant as in **1** and **2**. The somewhat larger ferromagnetic coupling observed in **1** can be explained in terms of the lower trigonal bipyramidal character of the copper(II) environment in this compound [$\tau = 0.016$ (**1**) and 0.18 (**2**)]. This causes a relatively greater d_{z^2} contribution to the magnetic orbital in **2** and thus a somewhat greater overlap between the magnetic orbitals in this compound would occur. J_{AF} is reinforced in **2** *vs.* **1** and consequently, the overall magnetic coupling is less ferromagnetic in the latter compound.

Summarizing, in the present contribution we show how the versatility of malonate as a ligand can afford new examples of uniform chains of copper(II) ions exhibiting intrachain ferromagnetic coupling through the carboxylate-malonate bridge. In the near future, higher dimensionality systems may be designed by substituting the peripheral ligand L [L = Im (**1**) and 2-MeIm (**2**)] by suitable bridging groups.[7a,9b]

Experimental

Materials

Malonic acid, potassium carbonate, copper(II) sulfate pentahydrate, imidazole and 2-methylimidazole were purchased from commercial sources and used as received. Elemental analyses (C, H, N) were performed on a EA 1108 CHNS-O microanalytical analyzer.

Synthesis of the complexes

[Cu(Im)$_2$(mal)]$_n$ (1). An aqueous solution of imidazole (5 mmol, 5 cm^3) was added to a warm aqueous solution of copper(II) sulfate pentahydrate (2.5 mmol, 20 cm^3). Potassium malonate (generated *in situ* by reacting stoichiometric amounts of malonic acid and potassium carbonate) dissolved in a minimum amount of water (2.5 mmol, 5 cm^3) was added to the previous warm purple-blue solution under continuous stirring. **1** separated as a purple-blue crystalline solid after one week. The product was purified by recrystallization from hot water. Prismatic purple-blue single crystals of **1** were obtained by slow evaporation of this solution at room temperature. Yield 0.528 g, 70%. Elem. anal. found: C, 35.68; H, 3.22; N, 18.38. Calcd. for $C_9H_{10}N_4O_4Cu$ (**1**): C, 35.82; H, 3.31; N, 18.57.

[Cu(2-MeIm)$_2$(mal)]$_n$ (2). This compound was prepared by following an analogous procedure to that of **1** but using 2-methylimidazole instead of imidazole. The shape and color of the crystals of **2** are the same as those of **1**. Yield 0.618 g, 75%. Elem. anal. found: C, 40.12; H, 4.14; N, 16.80. Calcd. for $C_{11}H_{14}N_4O_4Cu$ (**2**): C, 40.05; H, 4.24; N, 16.99.

Physical techniques

IR spectra (450–4000 cm^{-1}) of compounds **1** and **2** were recorded on a Bruker IF S55 spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility measurements on polycrystalline samples of **1** and **2** were carried out in the temperature range 1.9–290 K with a Quantum Design SQUID magnetometer operating at 100 G ($T < 50$ K) and 1000 G ($T > 50$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[24] as -130×10^{-6} (**1**) and -157×10^{-6} cm^3 mol^{-1} (**2**), respectively. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [60×10^{-6} cm^3 mol^{-1} per Cu(II)] and the magnetization of the sample holder.

Table 1 Crystallographic data for [Cu(Im)$_2$(mal)]$_n$ (**1**) and [Cu(2-MeIm)$_2$(mal)]$_n$ (**2**)

Compound	**1**	**2**
Formula	$C_9H_{10}O_4N_4Cu_1$	$C_{11}H_{14}O_4N_4Cu_1$
FW	301.75	329.80
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	7.791(2)	7.036(2)
b/Å	7.634(2)	8.230(2)
c/Å	19.364(4)	22.932(3)
β/deg	98.42(3)	90.0
u/Å^3	1139.3(5)	1327.9(5)
Z	4	4
T/K	293(2)	293(2)
μ(Mo Kα)/cm^{-1}	19.304	16.640
Indep. reflect.	3308	2230
Obs. reflect. [$I \geqslant 2\sigma(I)$]	2491	1810
R^a (all data)	0.069	0.071
$R_w{}^b$ (all data)	0.117	0.116
R^a [$I \geqslant 2\sigma(I)$]	0.0408	0.0408
$R_w{}^b$ [$I \geqslant 2\sigma(I)$]	0.1050	0.1047
R_{int}	0.0110	0.0027

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2]/\Sigma w|F_o|^2]^{1/2}$.

Crystallographic data collection and structure determination

Crystals of dimensions $0.45 \times 0.30 \times 0.20$ (**1**) and $0.60 \times 0.13 \times 0.10$ mm (**2**) were used for data collection on an Enraf–Nonius MACH3 four-circle diffractometer. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data of 25 reflections in the range $6 < \theta < 18°$.[25,26] Data were collected at 293(2) K using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) and the ω-scan technique. A summary of the crystallographic data and structure refinement is given in Table 1. Examination of three standard reflections, monitored every 2 h, showed no sign of crystal deterioration. All the measured independent reflections were used in the analysis. Intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structures of **1** and **2** were solved by direct methods followed by successive Fourier synthesis through SIR97.[27] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on F^2 by using the SHELXL97[28] computational program. The hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Full-matrix least-squares refinement was performed minimizing the function $w(|F_o|^2 - |F_c|^2)$ with $w = 1/[\sigma^2(F_o)^2 + mP^2 + nP]$ and $P = (F_o{}^2 + 2F_c{}^2)/3$ with $m = 0.0672$ (**1**) and 0.0609 (**2**) and $n = 0.4775$ (**1**) and 1.4324 (**2**). Analytical expressions of neutral scattering factors were used, and anomalous dispersion corrections were incorporated.[29] The final geometrical calculations and the graphical manipulations were carried out with PARST95[30] and PLATON[31]

Table 2 Selected bond lengths (Å) and angles (deg) for compound **1**[a,b]

Cu(1)–N(1)	1.999(2)	Cu(1)–O(3)	1.932(2)
Cu(1)–N(3)	1.981(2)	Cu(1)–O(2a)	2.394(2)
Cu(1)–O(1)	1.962(2)		
N(1)–Cu(1)–N(3)	92.5(1)	N(3)–Cu(1)–O(1)	87.2(1)
N(1)–Cu(1)–O(1)	172.9(1)	N(3)–Cu(1)–O(3)	173.9(1)
N(1)–Cu(1)–O(3)	87.3(1)	N(3)–Cu(1)–O(2a)	98.2(1)
N(1)–Cu(1)–O(2a)	94.5(1)	O(1)–Cu(1)–O(3)	92.2(1)
O(1)–Cu(1)–O(2a)	92.5(1)	O(3)–Cu(1)–O(2a)	87.8(1)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Symmetry code: (a) $3/2 - x$, $1/2 + y$, $1/2 - z$.

Table 3 Selected bond lengths (Å) and angles (deg) for compound **2**[a,b]

Cu(1)–N(1)	1.992(4)	Cu(1)–O(3)	1.973(4)
Cu(1)–N(3)	2.024(4)	Cu(1)–O(2a)	2.270(4)
Cu(1)–O(1)	1.961(3)		
N(1)–Cu(1)–N(3)	90.9(2)	N(3)–Cu(1)–O(1)	89.4(1)
N(1)–Cu(1)–O(1)	170.9(2)	N(3)–Cu(1)–O(3)	160.1(2)
N(1)–Cu(1)–O(3)	86.9(1)	N(3)–Cu(1)–O(2a)	99.1(1)
N(1)–Cu(1)–O(2a)	98.8(1)	O(1)–Cu(1)–O(3)	89.6(1)
O(1)–Cu(1)–O(2a)	90.2(1)	O(3)–Cu(1)–O(2a)	100.8(1)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Symmetry code: (a) $x-1/2$, $1/2-y$, $-z+2$.

programs, respectively. Selected interatomic bond distances and angles for **1** and **2** are listed in Tables 2 and 3, respectively.

CCDC reference numbers 193604 and 193605. See http://www.rsc.org/suppdata/nj/b2/b201849g/ for crystallographic files in CiF or other electronic format.

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