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Copper(II) succinate complexes with 1,2-di-4-pyridylethane and 1,3-di-4-pyridylpropane

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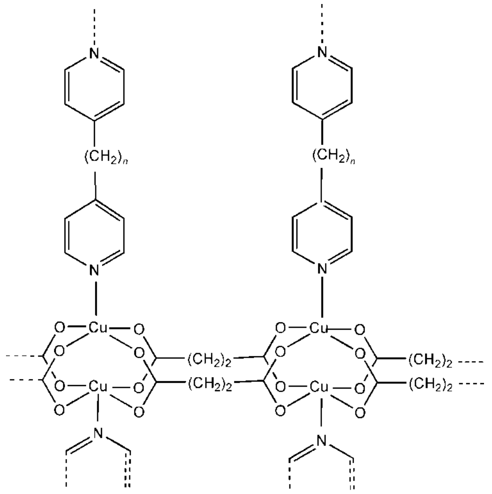
The compounds poly[di-μ_4-succinato-μ_2-1,2-di-4-pyridylethane-dicopper(II)], $[Cu_2(C_4H_4O_4)_2(C_{12}H_{12}N_2)]_n$, (I), and poly-[di-$\mu_4$-succinato-$\mu_2$-1,3-di-4-pyridylpropane-dicopper(II)], $[Cu_2(C_4H_4O_4)_2(C_{13}H_{14}N_2)]_n$, (II), exhibit polymeric structures with the dicopper units doubly bridged by bis-bidentate succinate groups and crosslinked by the separator bis(pyridyl) molecules. In (I), the molecule exhibits a centre of inversion located midway between the core Cu-dimer atoms and another that relates half of the bis(pyridyl)ethane ligand to the other half. Compound (II) has a similar molecular packing but with a doubled lattice constant and noncentrosymmetric core units. An antiferromagnetic interaction due to the dinuclear copper units was deduced from magnetic subsceptibility measurements, and spin triplet signals were detected in the electron paramagnetic resonance spectra for both compounds.

Comment

Metal–organic coordination polymers are of great current interest and spacer ligands are frequently used to form new extended framework structures. Dimetal units can be combined with bidentate organic ligands, such as 1,2-di-4-pyridylethane and 1,3-di-4-pyridylpropane, as flexible organic spacers to give rise to a large variety of structures (Batsanov *et al.*, 1996; Suen *et al.*, 2006; Carballo *et al.*, 2007). The resultant structures combining dimetal $Cu_2(OAc)_4$ units with two different *N*,*N*′-bidentate ligands, *viz.* 1,2-di-4-pyridylethane and 1,4-di-4-pyridylbuta-1,3-diyne, have been reported as one-dimensional polymeric chains containing a bridging nitrogenated ligand and dimeric $Cu_2(OAc)_4$ units (Goforth *et al.*, 2005). Besides the observed polymorphism due to the crystallization conditions, π–π interactions between the pyridyl rings play an important role in the resultant packing of the polymeric chains (Hu *et al.*, 2005).

During investigations of the magnetic properties of compounds based on copper(II) succinate complexes, two new compounds, (I) and (II), were synthesized with 1,2-di-4-pyridylethane and 1,3-di-4-pyridylpropane as bidentate ligands. Our goal was centred on the structural frameworks resulting from the interaction of the succinate chains with *N*,*N*′-bidentate spacer ligands. The structure of the binuclear unit was reported by O'Connor & Maslen (1966) for copper(II) succinate dihydrate, $[Cu(C_4H_4O_4)]\cdot 2H_2O$. In that structure, ribbon-like chains of paddle-wheel dicopper units are doubly bridged through bis-bidentate succinate groups. Each succinate anion links two dimeric units in the chain and two linking succinate anions are located between each pair of dimeric copper groups. A water molecule is coordinated to each Cu atom in the apical position.



(I) $n = 2$
(II) $n = 3$

The structures of both (I) and (II) are monoclinic $P2_1/c$ and can be described as ribbon-like chains of paddle-wheel dicopper units doubly bridged through bis-bidentate succinate groups in *gauche* conformations, with torsion angle C7—C8—C9—C10 = 67.6 (2)° in (I), and C1—C2—C3—C4 = 70.6 (6)° and C5—C6—C7—C8 = −62.47 (1)° in (II), similar to those found for $[Cu(C_4H_4O_4)]\cdot 2H_2O$ (O'Connor & Maslen, 1966). The molecular conformations are shown in Fig. 1 and the molecular packing, viewed along the [010] direction, is shown for both compounds in Fig. 2. The dimeric copper(II) units are coordinated through the two N atoms of the bridging ligands in infinite chains. The –Cu–Cu–py$(CH_2)_n$py–Cu–Cu– chains run along the [101] direction in (I) and along the [201] direction in (II). Parallel chains related by a unit-cell translation along [010] are linked by succinate groups and form two-dimensional sheets (Fig. 2*c*). In compound (I), the planes of the two pyridyl rings in the 1,2-di-4-pyridylethane ligand are parallel because the ligand sits across a centre of inversion. The pyridyl rings of chains of parallel sheets are symmetry related by the twofold screw axis, and those at (x, y, z) and ($1 - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$) form a dihedral angle of 27.7 (3)° with a relative disposition far from eclipsed because of the shift

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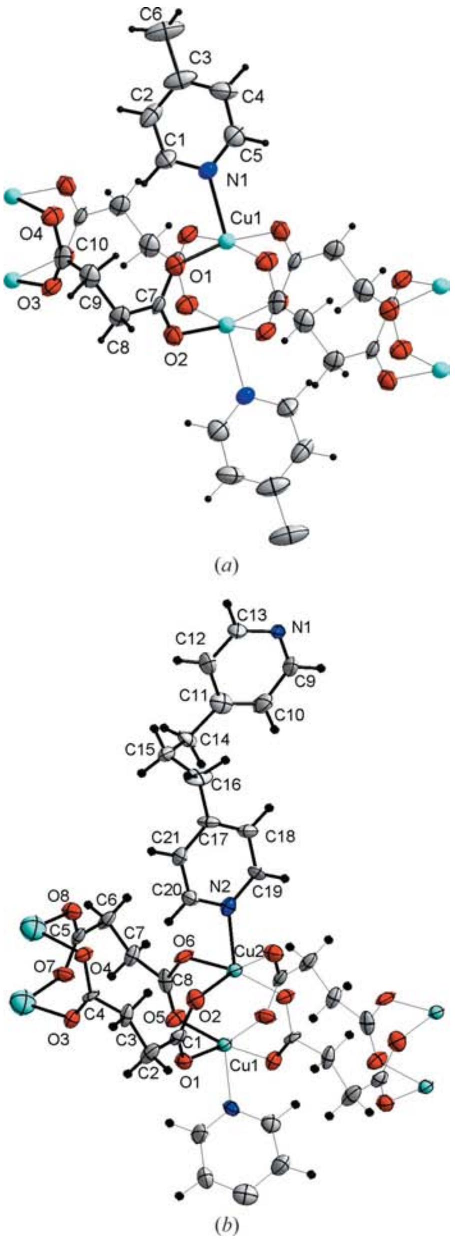

Figure 1
(*a*) A view of the copper coordination with a partial chain for (I) and (*b*) the configuration for compound (II). Atoms of the asymmetric units are labelled. For (I), the Cu···Cu vector is centred at $(0, 1, \frac{1}{2})$. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

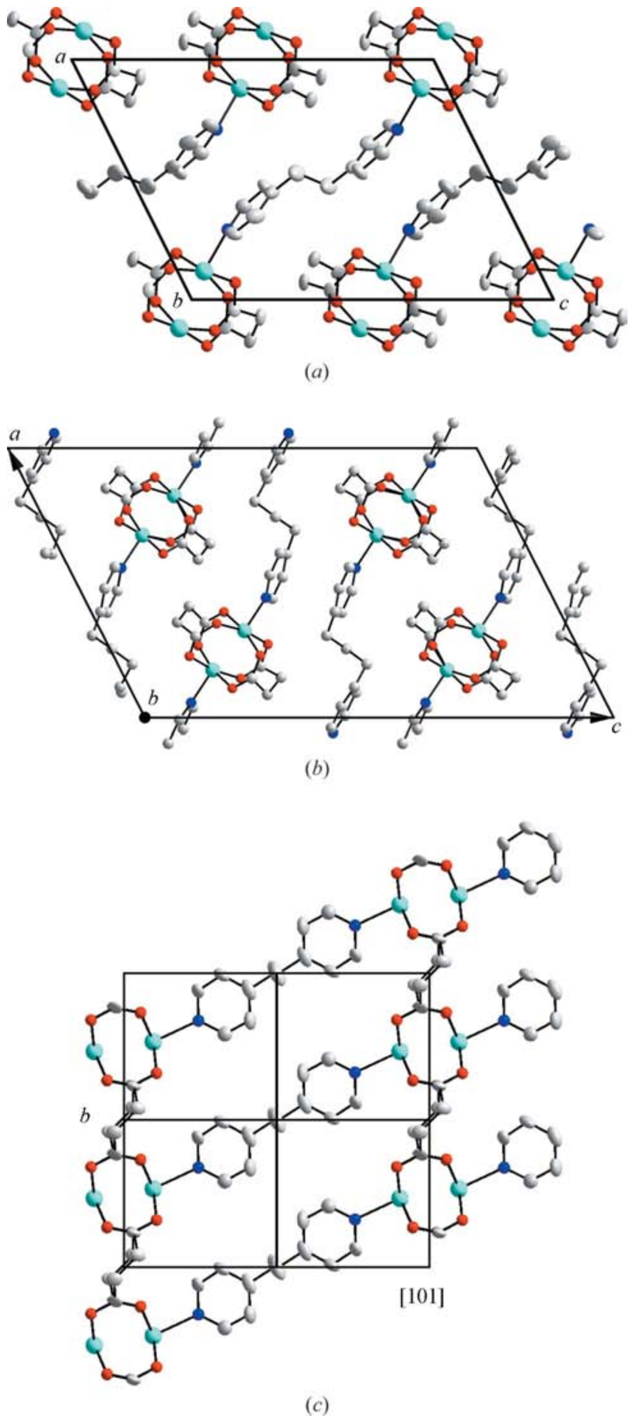

Figure 2
Projections along [010], showing the molecular packing of (*a*) (I) and (*b*) (II). H atoms have been omitted for clarity. (*c*) The two-dimensional network of parallel chains linked by succinate groups in (I); the network is similar in compound (II).

of $\frac{b}{2}$ [the $Cg\cdots Cg$ distance between their centroids is 4.783 (3) Å].

In compound (II), the pyridyl rings containing atoms N1 and N2 form a dihedral angle of 12.3 (3)° and exhibit two different interactions with the rings of parallel symmetry-related chains. For pairs of rings containing N1 at (x, y, z) and $(2 - x, 1 - y, 1 - z)$, the $Cg\cdots Cg$ distance is 3.761 (3) Å (slip distance = 1.29 Å), whereas for the rings containing N2 at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, these values are 3.631 (4) and 1.03 Å, respectively, which corresponds to a π–π interaction. In this way, the chains interact through these π–π stacking interactions between pyridyl ring pairs and a three-dimensional architecture is thereby established. Other such π–π interactions between pairs of aromatic rings have been described (Perlepes *et al.*, 1992).

In both compounds, each Cu^{II} atom exhibits the same coordination, *viz.* a square-pyramidal geometry. The geometry of the dinuclear unit is described in Tables 1 and 2 for compounds (I) and (II), respectively. The equatorial plane is formed by four O atoms of four succinate groups. The apical position is occupied by an N atom of a spacer ligand. The trigonality indices (Addison *et al.*, 1984) deduced from the angle data [τ = 0.004 for (I), and 0.005 (Cu1) and 0.004 (Cu2) for (II)] indicate a square-pyramidal geometry. The Cu^{II} atoms are displaced from the basal plane towards the apical N atom by 0.218 Å in (I), and by 0.195 (Cu1) and 0.213 Å (Cu2) in (II). This coordination geometry is similar to that found for copper(II) succinate dihydrate (O'Connor & Maslen, 1966). The magnetic and electron paramagnetic resonance (EPR) results for $[Cu(C_4H_4O_4)]\cdot 2H_2O$ (Sharrok & Melnik, 1985) correspond to the antiferromagnetic interaction characteristic of dimeric units with four *syn–syn* bridging carboxylate groups. We found similar results in compounds (I) and (II).

The magnetic and EPR results agree with those found for compounds containing a dimeric copper unit (Seco *et al.*, 2002; Sapiña *et al.*, 1994). A hypothetical interaction through the nitrogenated ligands is negligible, as in the case of the one-dimensional chains with 1,2-di-4-pyridylethane (Carballo *et al.*, 2007).

Experimental

A combined solution of $CuSO_4\cdot 5H_2O$ (0.125 mmol, 31 mg) and succinic acid (0.125 mmol, 15 mg) in H_2O (25 ml), 1,2-di-4-pyridylethane (0.125 mmol, 23 mg) in H_2O (25 ml) and urea (0.437 mmol, 26 mg) in H_2O (25 ml) was prepared. After approximately one month, small green crystals of (I) suitable for X-ray crystallographic study were obtained. Crystals of compound (II) were obtained by the same procedure, but using 1,3-di-4-pyridylpropane.

Temperature-dependent magnetic susceptibility data were collected in the 6.5–300 K range using a Quantum Design PPMS 6000 magnetometer in a field strength of 5 kOe. The $\chi_m\cdot T$ values decrease with decreasing temperature in the manner characteristic of paddle-wheel dinuclear copper groups. The observed $\chi_m\cdot T$ data were fitted to the Bleaney–Bowers equation for a dimer with $S_1 = S_2 = \frac{1}{2}$, modified by the inclusion of a fraction of monomeric impurity (O'Connor, 1982): $\chi_m(2Cu) = 2(\{C\exp(x)(1-\rho)/[1+3\exp(x)]\} + C\rho/4 + N\alpha)$, where $C = Ng^2\beta^2/kT$, $x = 2J/kT$, $2J$ is the separation between singlet and triplet states [g is the gyromagnetic factor, T is the temperature, k the Boltzman constant, ρ is the fraction of monomeric impurity and $N\alpha$ is the temperature-independent paramagnetism (TIP)]. The antiferromagnetic parameters are $2J = -366$ and -336 cm^{-1} for (I) and (II), respectively. The powder EPR spectra of (I) and (II), recorded on a Bruker ESP 300 spectrometer at Q band 33.5 GHz and room temperature, show the five signals of the triplet state ($S = 1$) for $D \neq 0$ and $E \simeq 0$. The spectra were interpreted according to the Wasserman, Snyder and Yager equations (Bencini & Gatteschi, 1990). The values $g_{\rm parallel} = 2.26/2.26$, $g_{\rm perpendicular} = 2.07/2.06$ and $D = 0.36/0.37$ cm^{-1} for (I)/(II) were thereby obtained.

Compound (I)

Crystal data

$[Cu_2(C_4H_4O_4)_2(C_{12}H_{12}N_2)]$
$M_r = 271.7$
Monoclinic, $P2_1/c$
$a = 11.342$ (2) Å
$b = 6.4613$ (10) Å
$c = 15.269$ (4) Å
$\beta = 116.55$ (3)°
$V = 1000.9$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.18$ mm^{-1}
$T = 295$ K
0.16 × 0.16 × 0.02 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
Absorption correction: integration (*JANA2006*; Petříček *et al.*, 2006) $T_{\rm min} = 0.763$, $T_{\rm max} = 0.960$
10503 measured reflections
2885 independent reflections
1225 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.093$

Refinement

$R[F > 2\sigma(F)] = 0.058$
$wR(F) = 0.068$
$S = 0.99$
2885 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 1.83$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.97$ e Å^{-3}

Compound (II)

Crystal data

$[Cu_2(C_4H_4O_4)_2(C_{13}H_{14}N_2)]$
$M_r = 557.5$
Monoclinic, $P2_1/c$
$a = 15.5630$ (10) Å
$b = 6.4472$ (7) Å
$c = 24.100$ (2) Å
$\beta = 116.913$ (9)°
$V = 2156.2$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.03$ mm^{-1}
$T = 295$ K
0.29 × 0.08 × 0.02 mm

Data collection

Stoe IPDS image-plate diffractometer
Absorption correction: Gaussian (*JANA2006*; Petříček *et al.*, 2006) $T_{\rm min} = 0.789$, $T_{\rm max} = 0.960$
25854 measured reflections
5101 independent reflections
1931 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.110$

Refinement

$R[F > 2\sigma(F)] = 0.056$
$wR(F) = 0.054$
$S = 1.30$
5101 reflections
248 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.54$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.85$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1···Cu1^{i}	2.665 (2)	Cu1—O4^{ii}	1.955 (5)
Cu1—O1	1.955 (4)	Cu1—O3^{iii}	1.983 (5)
Cu1—O2^{i}	1.967 (4)	Cu1—N1	2.218 (4)
O1—Cu1—O2^{i}	167.08 (15)	O2^{i}—Cu1—O4^{ii}	89.86 (19)
O1—Cu1—O4^{ii}	88.93 (19)	O2^{i}—Cu1—O3^{iii}	88.83 (19)
O1—Cu1—O3^{iii}	89.57 (19)	O4^{ii}—Cu1—O3^{iii}	167.50 (15)

Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $x, y+1, z$; (iii) $-x, -y+1, -z+1$.

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1···Cu2	2.6336 (17)	Cu2—O2	1.971 (9)
Cu1—O1	1.968 (9)	Cu2—O4^{i}	1.989 (9)
Cu1—O3^{i}	1.967 (9)	Cu2—O6	1.974 (9)
Cu1—O5	1.953 (9)	Cu2—O8^{i}	1.963 (9)
Cu1—O7^{i}	1.957 (9)		
O1—Cu1—O3^{i}	89.0 (4)	O2—Cu2—O4^{i}	88.5 (4)
O1—Cu1—O5	89.3 (4)	O2—Cu2—O6	89.9 (4)
O1—Cu1—O7^{i}	168.1 (3)	O2—Cu2—O8^{i}	167.9 (3)
O3^{i}—Cu1—O5	169.3 (3)	O4^{i}—Cu2—O6	167.6 (3)
O3^{i}—Cu1—O7^{i}	89.9 (4)	O4^{i}—Cu2—O8^{i}	90.1 (4)
O5—Cu1—O7^{i}	89.6 (4)	O6—Cu2—O8^{i}	88.9 (4)

Symmetry code: (i) $x, y-1, z$.

The space group for both (I) and (II) is $P2_1/c$, but the lattice constants cannot be compared directly. The relationship between the cell parameters is given by $a_{\rm I} = 1/2c_{\rm II}$, $b_{\rm I} = b_{\rm II}$ and $c_{\rm I} = a_{\rm II} + 1/2c_{\rm II}$. The diffraction pattern of (II) shows a pseudo-body-centred symmetry ($h + k + l = 2n$) which, combined with the genuine conditions for $P2_1/c$, gives pseudo-conditions for $I2/a$ (standard $C2/c$). For both compounds, the H-atom coordinates were calculated with C—H = 0.98 Å and constrained, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The atomic displacement parameters of the pyridyl rings indicate some orientational disorder, with a large component of the thermal ellipsoid perpendicular to the plane of the ring.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007) for (I); *X-AREA* (Stoe & Cie, 2006) for (II). Cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007) for (I); *X-AREA* for (II). Data reduction: *CrysAlis RED* for (I); *X-RED32* (Stoe & Cie, 2006) for (II). For both compounds, program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3201). Services for accessing these data are described at the back of the journal.

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