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Synthesis, structure and magnetic properties of cobalt(II) and copper(II) coordination polymers assembled by phthalate and 4-methylimidazole

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Abstract

New coordination polymers $[M(Pht)(4\text{-MeIm})_2(H_2O)]_n$ (M = Co (**1**), Cu (**2**); Pht^{2-} = dianion of o-phthalic acid; 4-MeIm = 4-methylimidazole) have been synthesized and characterized by IR spectroscopy, X-ray crystallography, thermogravimetric analysis and magnetic measurements. The crystal structures of **1** and **2** are isostructural and consist of $[M(4\text{-MeIm})_2(H_2O)]$ building units linked in infinite 1D helical chains by 1,6-bridging phthalate ions which also act as chelating ligands through two O atoms from one carboxylate group in the case of **1**. In complex **1**, each Co(II) atom adopts a distorted octahedral N_2O_4 geometry being coordinated by two N atoms from two 4-MeIm, three O atoms of two phthalate residues and one O atom of a water molecule, whereas the square-pyramidal N_2O_3 coordination of the Cu(II) atom in **2** includes two N atoms of N-containing ligands, two O atoms of two carboxylate groups from different Pht, and a water molecule. An additional strong O–H···O hydrogen bond between a carboxylate group of the phthalate ligand and a coordinated water molecule join the 1D helical chains to form a 2D network in both compounds. The thermal dependences of the magnetic susceptibilities of the polymeric helical Co(II) chain compound **1** were simulated within the temperature range 20–300 K as a single ion case, whereas for the Cu(II) compound **2**, the simulations between 25 and 300 K, were made for a linear chain using the Bonner–Fisher approximation. Modelling the experimental data of compound **1** with MAGPACK resulted in: $g = 2.6$, $|D| = 62\,\text{cm}^{-1}$. Calculations using the Bonner–Fisher approximation gave the following result for compound **2**: $g = 2.18$, $J = -0.4\,\text{cm}^{-1}$.
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1. Introduction

Inorganic coordination polymers or solid-state polymers have received considerable attention in the past few years due to possible applications as new materials in catalysis, adsorption, ion exchange, separation, magnetic devices, etc. (for recent reviews see [1]). Metal coordination polymers containing dicarboxylate ions as the organic spacer have been the subject of particular interest not only because of their fascinating architec-

tures, but also due to their advantageous properties such as bulk magnetic behavior, high dimensionality, optical activity and thermal stability. In particular, coordination polymers with terephthalic [2], isophthalic [3] and phthalic acids [4–31] have been extensively studied. Among these isomeric forms the o-phthalate ligand, with two carboxylic groups in *ortho*-position, can adopt the most diverse bonding modes (26 coordination modes [32]) in metal complexes. As a result, it can be expected that more complicated and unexpected architectures leading to new properties and reactivity can be constructed. We have recently become interested in the synthesis of 3d-coordination compounds with the

phthalate and N-containing ligands. Copper(II) [32–33], cobalt(II) [32,34], and zinc(II) [32,35–36] coordination polymers have been reported so far. In an extension of the study here we report on the synthesis, crystal structure and magnetic properties of new cobalt(II) and copper(II) mixed-ligand coordination polymers $[M(Pht)(4\text{-MeIm})_2(H_2O)]_n$ (where Pht^{2-} = dianion of *o*-phthalic acid, 4-MeIm = 4-methylimidazole).

2. Experimental

2.1. Materials and methods

All the starting materials were reagent grade and used as purchased. The infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrometer using KBr pellets in the region 4000–400 cm^{-1}. Thermogravimetric analyses were carried out in dry nitrogen (60 mL/min) at a heating rate of 5°C/min from room temperature (r.t.) to 600°C on a Mettler-Toledo TA 50 instrument.

2.2. Synthesis

2.2.1. [Co(Pht)(4-MeIm)₂(H₂O)]ₙ (1)

A solution of $Co(O_2CMe)_2 \cdot 4H_2O$ (1.24 g, 5 mmol) in water (10 mL) was added to a hot solution of KHPht (1.02 g, 5 mmol) and 4-MeIm (0.82 g, 10 mmol) in water (10 mL). The resulting mixture was stirred and heated for 30 min and left to stand overnight at r.t. The dark red crystalline product was filtered off, washed with water and ethanol and dried in air. Yield: 1 g, 50%. An additional batch of **1** can be obtained by keeping the mother filtrate in air over 2 weeks (yield ca. 20%). *Anal.* Calc. for $C_{16}H_{18}CoN_4O_5$: C, 47.42%; H, 4.48%; N, 13.82%. Found: C, 47.94%; H, 4.54%; N, 13.81%. IR data (KBr, cm^{-1}): 3414s,br, 3211s, 3008sh, 1596sh, 1559vs,br, 1493s, 1446s, 1417vs, 1396vs, 1259w, 1234w, 1158w, 1108m, 1088w, 962m, 870sh, 840m, 816m, 770m, 725m, 701m, 662s, 624w, 584m. Single crystals suitable for diffraction studies were obtained by recrystallization of **1** from hot aqueous solution.

2.2.2. [Cu(Pht)(4-MeIm)₂(H₂O)]ₙ (2)

A solution of $Cu(O_2CMe)_2 \cdot H_2O$ (1 g, 5 mmol) in water (10 mL) was added to a warm solution of *o*-phthalic acid (0.83 g, 5 mmol) and 4-MeIm (0.82 g, 10 mmol) in water (30 mL). The resulting mixture was stirred and heated for 30 min. The blue microcrystalline precipitate was filtered off, washed with water and ethanol and dried in air. Yield: 1.3 g, 64.2%. *Anal.* Calc. for $C_{16}H_{18}CuN_4O_5$: C, 46.88%; H, 4.43%; N, 13.67%. Found: C, 46.2%; H, 4.37%; N, 13.2%. IR data (KBr, cm^{-1}): 3430s,br, 3145br, 3004sh, 1604sh, 1584sh, 1552vs,br, 1502s, 1489s, 1446sh, 1434s, 1407vs, 1396vs, 1261w, 1238w, 1160w, 1110s, 1088w, 971m, 852m,

817m, 767m, 722m, 701w, 657s, 621m, 561w. Single crystals suitable for diffraction studies were obtained by recrystallization of **2** from hot aqueous solution.

2.3. Crystal structure determination

Single crystal X-ray diffraction data for **1** and **2** were collected on a Stoe Mark II—Imaging Plate Diffractometer System [37] equipped with a two-circle goniometer and using Mo$K\alpha$ graphite-monochromated radiation at 153 K. Image plate distance 100 mm, ω rotation scans 0–180° at ϕ 0°, and 0–35° at 90°, step $\Delta\omega = 1.2°$, 2θ range 2.29–59.53°, d_{max}–d_{min} = 17.799–0.716 Å. The crystallographic data and details on the refinements for **1** and **2** are summarized in Table 1. The structures were solved by direct methods using the programme SHELXS-97 [38]. The refinement and all further calculations were carried out using SHELXL-97 [39]. The H-atoms were located from Fourier difference maps and refined isotropically. The water molecule H-atoms were also located from difference maps but were held fixed with $U_{iso} = 1.5(U_{eq}$–O–atom) Å^2. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. Selected bond lengths and angles for **1** and **2** are listed in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 234706 (**1**), 234707 (**2**). Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

2.4. Magnetic measurements

Magnetic susceptibility data of powdered samples were collected on a MPMS Quantum Design SQUID magnetometer (XL-5) in the temperature range of 300–1.8 K and at a field of 1000 G. The samples were placed in a gelatine capsule and a straw was used as the sample holder. The output data were corrected for the experimentally determined diamagnetism of the sample holder and the diamagnetism of the sample calculated from Pascal's constants. The Levenberg–Marquardt least-squares fitting algorithm, in combination with MAGPACK [40], was used to model the experimental magnetic susceptibility data.

3. Results and discussion

3.1. Synthesis and preliminary characterization

Reaction of metal(II) acetate with 4-MeIm and KHPht or H$_2$Pht in water in a 1:2:1 mole ratio under heating leads to formation of polymers

Table 1
Crystal data and details of structural determinations

	1	2
Empirical formula	$C_{16}H_{18}CoN_4O_5$	$C_{16}H_{18}CuN_4O_5$
Formula weight	405.27	409.88
Temperature (K)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073
Crystal size (mm)	$0.40 \times 0.40 \times 0.40$	$0.40 \times 0.20 \times 0.15$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.4507(9)	11.6836(15)
b (Å)	9.1139(5)	9.0050(8)
c (Å)	16.3485(12)	16.504(2)
β (deg)	100.178(6)	100.159(10)
V (Å^3)	1679.3(2)	1709.2(3)
Z	4	4
D_c (g/cm^3)	1.603	1.593
μ (mm^{-1})	1.059	1.314
$F(000)$	836	844
θ range for data coll. (deg)	2.01–29.53	1.98–29.65
Index ranges	$-15 \leqslant h \leqslant 15$, $-11 \leqslant k \leqslant 12$, $-22 \leqslant l \leqslant 22$	$-14 \leqslant h \leqslant 16$, $-12 \leqslant k \leqslant 10$, $-22 \leqslant l \leqslant 22$
Reflections measured	20538	20538
Independent reflections	4647 [R(int) = 0.0494]	4647[R(int) = 0.0494]
Data/restraints/parameters	4647/0/300	4654/0/300
Goodness-of-fit on F^2	1.051	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0284$ $wR_2 = 0.0745$	$R_1 = 0.04212$ $wR_2 = 0.0936$
R indices (all data)	$R_1 = 0.0321$ $wR_2 = 0.0763$	$R_1 = 0.0673$ $wR_2 = 0.1042$
Largest diff. peak and hole (e/Å^3)	0.509 and -0.505	0.465 and -0.525

$[M(Pht)(4\text{-MeIm})_2(H_2O)]_n$ ($M = Co$ (**1**) and Cu (**2**)) in ca. 70% and 64% yields, respectively. The IR spectra of these compounds exhibit very strong bands in the 1604–1552 and 1417–1396 cm^{-1} regions due to the asymmetric and symmetric stretching vibrations of the coordinated carboxylate groups of the phthalate ligand, respectively [41–43]. The peaks that appeared at 3211–3145 cm^{-1} can be attributed to the N–H stretching vibration of 4-MeIm. The presence of coordinated water molecules in **1** and **2** caused the appearance of broad absorption bands with maxima at 3414 and 3430 cm^{-1}, respectively. Thermogravimetric analyses of the polymers performed in the range 25–600°C indicate that these coordinated water molecules are lost first between 100–190°C for **1** and 80–150°C for **2**. The weight losses of 4.59% and 4.57%, respectively, are close to the theoretical values (4.47% and 4.4%) for the removal of one water molecule per formula unit. On further heating, **1** lost weight between 200°C and 320°C corresponding to one 4-MeIm ligand (observed 18.18%, calculated 20.16%), then from 320°C to 520°C complex **1** decomposes abruptly to give the oxide CoO (found 20.30%, calculated 18.49%). The decomposition of the organic

moieties of **2** started at lower temperature (ca. 180°C) and was then followed by a two-step total weight loss of 61.68% from 180°C to 300°C, which is due to the loss of two molecules of 4-MeIm and one molecule of phenyl radical [44] (calculated 58.63%). Further weight loss of 13.53%, corresponding to the elimination of two molecules of CO [45] (calculated 13.67%), occurred between 420°C and 530°C. The final product is CuO with the remaining percentage of 20.28% (calculated 19.40%).

3.2. Crystal structures

3.2.1. $[Co(Pht)(4\text{-MeIm})_2(H_2O)]_n$ (**1**)

X-ray structural analysis reveals that **1** consists of $[Co(4\text{-MeIm})_2(H_2O)]$ entities linked by bridging phthalate anions into an infinite polymeric helical chain (Fig. 1). Each cobalt atom in **1** has a distorted octahedral (N$_2$O$_4$) coordination geometry with two nitrogen atoms N(1) and N(3) from two 4-MeIm moieties (Co(1)–N(1) 2.092(1), Co(1)–N(3) 2.087(1) Å), two oxygen atoms O(3a) and O(1w) belonging to the phthalate moiety (Co(1)–O(3a) 2.126(1) Å) and a water molecule

Table 2
Selected bond distances (Å) and angles (deg)

1		**2**	
Bond distances			
Co(1)–N(1)	2.092(1)	Cu(1)–N(1)	1.978(2)
Co(1)–N(3)	2.087(1)	Cu(1)–N(3)	1.981(2)
Co(1)–O(1w)	2.113(1)	Cu(1)–O(1w)	2.040(2)
Co(1)–O(3a)	2.126(1)	Cu(1)–O(3a)	2.009(2)
Co(1)–O(1)	2.129(1)	Cu(1)–O(1)	2.353(2)
Co(1)–O(4a)	2.261(1)	Cu(1)–O(4a)	2.630(2)
Bond angles			
N(3)–Co(1)–N(1)	177.18(4)	N(3)–Cu(1)–N(1)	177.65(9)
N(3)–Co(1)–O(1w)	86.94(4)	N(3)–Cu(1)–O(1w)	87.94(8)
N(1)–Co(1)–O(1w)	88.68(4)	N(1)–Cu(1)–O(1w)	89.98(8)
N(3)–Co(1)–O(3a)	91.66(4)	N(3)–Cu(1)–O(3a)	91.85(8)
N(1)–Co(1)–O(3a)	91.16(4)	N(1)–Cu(1)–O(3a)	90.41(8)
O(1w)–Co(1)–O(3a)	169.98(4)	O(1w)–Cu(1)–O(3a)	167.96(8)
N(3)–Co(1)–O(1)	88.64(4)	N(3)–Cu(1)–O(1)	88.20(8)
N(1)–Co(1)–O(1)	91.10(4)	N(1)–Cu(1)–O(1)	90.72(8)
O(1w)–Co(1)–O(1)	93.29(4)	O(1w)–Cu(1)–O(1)	90.56(8)
O(3a)–Co(1)–O(1)	96.73(3)	O(3a)–Cu(1)–O(1)	101.47(7)
N(3)–Co(1)–O(4a)	94.41(4)		
N(1)–Co(1)–O(4a)	86.93(4)		
O(1w)–Co(1)–O(4a)	110.04(4)		
O(3a)–Co(1)–O(4a)	59.94(3)		
O(1)–Co(1)–O(4a)	156.50(3)		

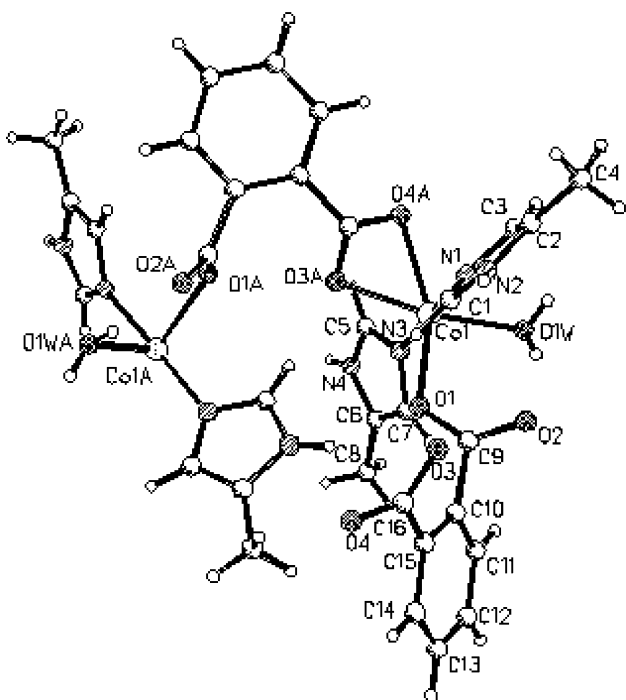Symmetry transformations used to generate equivalent atoms: $a - x + 1/2, y - 1/2, -z + 1/2$.

Fig. 1. The fragment of a polymeric chain in compound **1**.

(Co(1)–O(1w) 2.113(1) Å), that comprise the equatorial plane. The axial positions are filled by the remaining carboxylato-oxygen atom O(4a) of the Pht residue (Co(1)–O(4a) 2.261(1) Å) and the oxygen atom O(1) of the second Pht ligand (Co(1)–O(1) 2.129(1) Å). The Co–N distances are slightly shorter than Co–O distances, but all distances are comparable with those of other Co(II) complexes, containing as *co*-ligands both carboxylate and imidazole or its derivatives (Co–N 2.013(1)–2.069(1) Å and Co–O 1.962(1)–2.145(2) Å [34,46,47]), with the exception of the axial Co–O(4a)$_{carboxylate}$ distance, which is longer. The *trans* angles around the Co center range from 156.50(3)° to 177.18(4)°, whereas the *cis* angles range from 59.94(3)° to 110.04(4)° (Table 2). The main distortion from the octahedral geometry in the coordination polyhedron is due to the small angle O(3a)–Co(1)–O(4a) of 59.94(3)° at the chelate carboxylate group of the Pht ligand. This distortion is common for carboxylate groups acting in the 1,3-chelating manner and it was found, e.g., in [Cu(HPht)$_2$Py$_2$] (58.00(1)°) and [Cu(HPht)$_2$(γ-Pic)$_2$] (58.10(2)°) [33], [Zn(Pht)(γ-Pic)]$_n$ (57.11(1)°) [35]. The Pht^{2-} anion in this complex behaves as a tridentate ligand using one carboxylate group to coordinate to the Co(II) atom in a monodentate coordination fashion and the other carboxylate group to ligate the adjacent metal in a 1,3-chelating mode. The C–O bond distances of the carboxylate groups are in the range of 1.248(2)–1.268(1) Å and the O–C–O angle for monodentate carboxylate group is 125.45(11)°, slightly greater than 120.71(11)° for the chelating one. The dihedral angles between the carboxylate plane described by atoms O(1)C(9)O(2) and O(3)C(16)O(4) and aromatic ring of

the phthalate anion are 104.8(2)° and 30.6(2)°, respectively.

The most interesting feature of compound **1** is the formation of a helical structure. The Pht ligands bridge cobalt atoms forming an infinite 1D helical chain running along the [101] direction in the unit cell (Fig. 2). As shown in Fig. 3, one helical chain in compound **1** exhibits right handedness (a) while the adjacent chain is left handed (c). Because left-handed and right-handed helical chains coexist in the crystal structure (Fig. 3b),
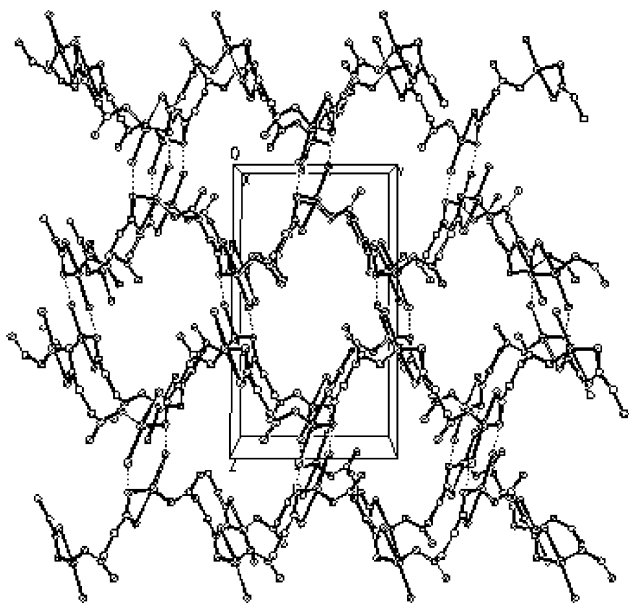
Fig. 2. Crystal packing of the 1D helical chains in **1**. The hydrogen atoms and cyclic fragments are omitted for clarity. Hydrogen bonds are shown as dotted lines.
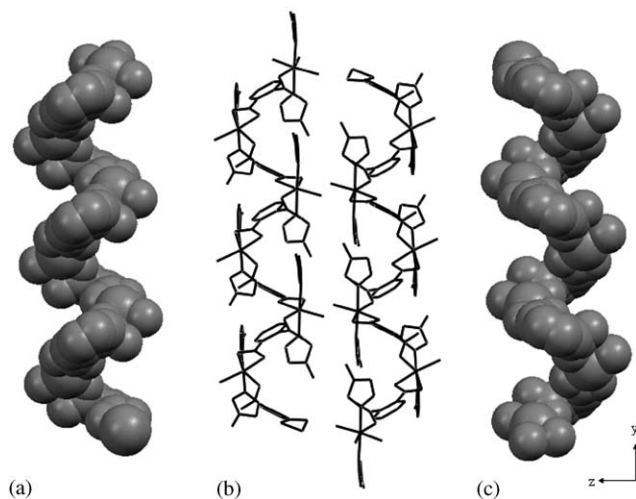
Fig. 3. A space-filling representation of the (a) right-handed chain, and (c) left-handed chain. Hydrogen atoms and 4-methylimidazole fragments are omitted for clarity. (b) A view of the crystallographic xy plane in **1**.

the whole crystal does not demonstrate chirality. Similar helical structures with the bridging phthalate ligand have been found in the zinc(II) mixed-ligand phthalate complexes $[Zn(Pht)(tu)_2]_n$ [25] and $[Zn(Pht)(bpy)(H_2O)]_n$ [31]. The intra-helix Co···Co separation is 6.247(1) Å, longer than that in the helix of $[Zn(Pht)(bpy)(H_2O)]_n$ (5.633 Å [31]) but shorter than the corresponding metal···metal distance of 7.367(1) Å found in the linear chain of $[Co(Pht)(2\text{-}MeIm)_2]_n$ [34]. It is interesting to note that each phthalate ligand is further involved in strong O–H···O hydrogen bonding with the coordinated water molecule (O(1w)–H(1)···O(4) = 2.722(1) Å). This hydrogen bond links the adjacent helixes, as illustrated in Figs. 2 and 4, forming layers along the [101] direction. The nearest inter-helix Co···Co distance is 5.164(1) Å. There are also two additional N–H···O interactions between the carboxylate oxygens (O(1) and O(2)) of the phthalate and uncoordinated nitrogens (N(2) and N(4)) from 4-MeIm molecules (N(2)···O(1) = 2.872(1) Å and N(4)···O(2) = 2.799(1) Å) and one O–H···O contact involving coordinated H_2O (O(1w)···O(2) = 2.697(1) Å) within the helical chains. Corresponding hydrogen bonding data are given in Table 3.

3.2.2. $[Cu(Pht)(4\text{-}MeIm)_2(H_2O)]_n$ (**2**)

The structure of **2** is similar to **1** and consists of a polymeric helical chain of repeating $[Cu(4\text{-}MeIm)_2(H_2O)]$ building units linked together via the phthalate anions (Fig. 5). Each copper atom is coordinated by a pair of 4-MeIm units, a pair of phthalate ligands and a water molecule; however, two o-phthalate ions are ligated to a Cu(II) atom through carboxylate oxygen in a monodentate fashion. As a consequence, a square-pyramidal N_2O_3 coordination geometry is observed around the Cu(II) atom. The basal plane of the $\{CuN_2O_3\}$ square pyramid is defined by N(1) and N(3) from the 4-MeIm molecules, and O(3a) and O(1w) of the carboxylate group and water molecule. The apical position is occupied by O(1) of the carboxylate group belonging to another Pht residue. The equatorial Cu–N (1.978(2), 1.981(2) Å), Cu–$O_{carboxylate}$ (2.009(2) Å) and Cu–O_{water} (2.040(2) Å) distances are in agreement with those observed in $[Cu_2(Pht)_2(\gamma\text{-}Pic)_4(H_2O)]_n$ (Cu–N 1.985(7)–2.012(7), Cu–O 1.995(7)–2.053(5) Å [33]). The axial Cu(1)–O(1) distance of 2.353(2) Å is longer than that in the related complex (2.240(4) Å [33]). The bond angles at Cu atom range from 87.94(8)° to 101.47(7)° (Table 2).

The Pht^{2-} anion behaves as a bidentate ligand bridging two adjacent Cu(II) atoms through oxygen atoms from both carboxylate groups (1,6-bridging mode). The C(9)–O(1) and C(16)–O(3) bond distances of the carboxylate groups are similar or slightly longer (1.253(3) and 1.268(3) Å, respectively) than the C(9)–O(2) and C(16)–O(4) distances of 1.254(3) and
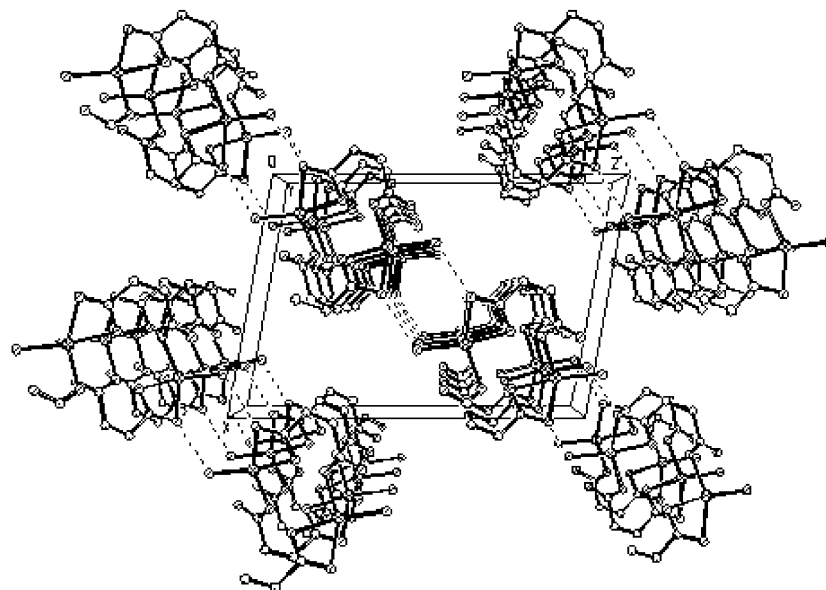
Fig. 4. A perspective view of the 1D helical chains in the crystal structure of **1** along *y*-axis. The hydrogen atoms and cyclic fragments are omitted for clarity. Hydrogen bonds are shown as dotted lines.

Table 3
Hydrogen bonding interactions

D–H···A	d(D–H) (Å)	d(H···A) (Å)	angle DHA (deg)	d(D···A) (Å)
1				
N(2)–H(2)···O(1)[a]	0.88	2.061	152	2.872(1)
N(4)–H(4)···O(2)[b]	0.88	1.927	170	2.799(1)
O(1w)–H(1a)···O(4)[c]	0.83(2)	1.90(2)	171(3)	2.722(1)
O(1w)–H(1b)···O(2)	0.84(3)	1.92(3)	155(3)	2.697(1)
2				
N(2)–H(2)···O(1)[a]	0.88	2.013	153	2.826(3)
N(4)–H(4)···O(2)[b]	0.88	1.901	171	2.772(3)
O(1w)–H(1a)···O(4)[c]	0.78(6)	1.90(5)	170(6)	2.676(3)
O(1w)–H(1b)···O(2)	0.84(4)	1.89(4)	155(4)	2.673(3)

[a] $1/2 - x, y + 1/2, 1/2 - z$.
[b] $x, y - 1, z$.
[c] $1/2 + x, 1/2 - y, 1/2 + z$.

1.247(3) Å, respectively, which do not take part in coordination to metal ions. The C–C bond distances, being between 1.372(5) and 1.400(3) Å, and the C–C–C angles of the aromatic ring of the Pht molecules, varying from 118.9(3)° to 121.0(3)°, fall in the range of values found in the pure ligand [48] and in **1** or other complexes [33,34]. The dihedral angles formed between the carboxylate plane and the aromatic ring in the phthalate anion are 106.5(2)° for O(1)C(9)O(2) and 28.0(2)° for O(3)C(16)O(4), quite similar to those found in **1**.

As in **1**, the phthalate ligand links the [Cu(4-MeIm)$_2$(H$_2$O)] units into an infinite helical chain along the [110] direction in the unit cell of **2**. The intra-helix Cu···Cu distance is 6.254(1) Å which is comparable to the intra-helix Co···Co distance in **1** (6.247(1) Å). The

polymeric helical chains are knitted together by O–H···O hydrogen bonds between the oxygen O(4) atom of the carboxylate and the hydrogen atom of coordinated water molecules (O(1w)–H···O(4) = 2.676(3) Å) to create 2D layers parallel to the [101] direction in the unit cell. Between the adjacent helixes the shortest Cu···Cu distance is 5.251(1) Å. Additional strong O–H···O hydrogen bonds between a coordinated water molecule and uncoordinated carboxylate oxygen atoms O(2) (O(1w)···O(2) = 2.673(3) Å) and N–H···O bonds involving uncoordinated 4-methylimidazole nitrogen atoms (N(2) and N(4)) and oxygen atoms (O(1) and O(2)) of the phthalate of 2.826(3) and 2.772(3) Å, respectively, were found within the helixes. Corresponding hydrogen bonding data are given in Table 3.

3.3. Magnetic properties

The thermal dependence of $\chi_M T$ ($\chi_M T$ being the product of the molar magnetic susceptibility and the temperature) and the simulated curves for powdered samples of the polymeric helical chain compounds **1** and **2** are shown in Figs. 6 and 7. The molar magnetic susceptibilities have been corrected for their diamagnetic and temperature independent paramagnetic (TIP) con-
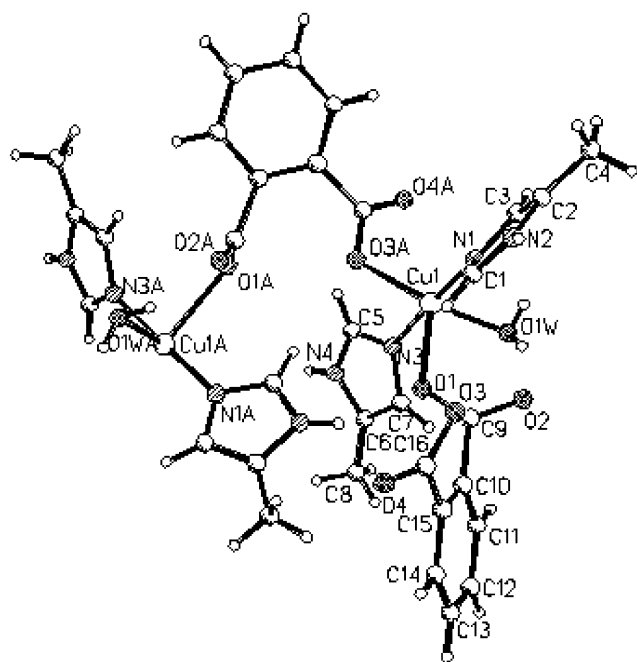
Fig. 7. Temperature dependence of $\chi_M T$ for compound **2**. The circles correspond to the experimental data, the simulation for the linear chain model is depicted as a line.

Fig. 5. The fragment of polymeric chain in compound **2**.

tributions. For compound **1**, the TIP is 4.6×10^{-4} emu/mol. The room temperature $\chi_M T$ value of 3.16 emu K/mol for compound **1** (Fig. 6) agrees well with the calculated value of 3.17 emu K/mol for a high-spin Co(II) compound ($S = 3/2$, $g = 2.6$) [49]. The gradual decrease of $\chi_M T$ by lowering the temperature is typical for high-spin Co(II). This decrease of $\chi_M T$ is due to zero-field splitting. A simulation within the temperature range 20–300 K with a g-value of 2.6 and an axial zero-field splitting parameter of $|D| = 62$ cm^{-1} agrees best with the experimental data. The $\chi_M T$ values of compound **2**, with a TIP of 0.6×10^{-4} emu/mol, remain constant at 0.44 emu K/mol down to 50 K (Fig. 7). This agrees well with the calculated $\chi_M T$ value of 0.41 emu K/mol for a single Cu(II) ion ($S = 1/2$, $g = 2.1$) [50]. Below 50 K, $\chi_M T$ decreases due to a weak intramolecular antiferromagnetic interaction of neighboring Cu(II) ions in the chain. Below 25 K, probably weak intermolecular ferromagnetic interactions between Cu(II) ions of neighboring chains provoke an increase of $\chi_M T$. With the Bonner–Fisher model [51], for which the interaction is approximated as one between the Cu(II) ions in a linear, equally spaced chain, the experimental data, between 25 and 300 K, could be simulated best with $g = 2.18$ and $J = -0.4$ cm^{-1}.
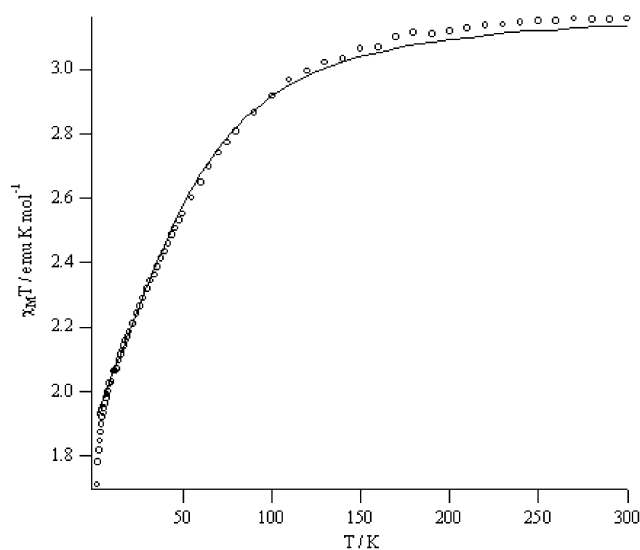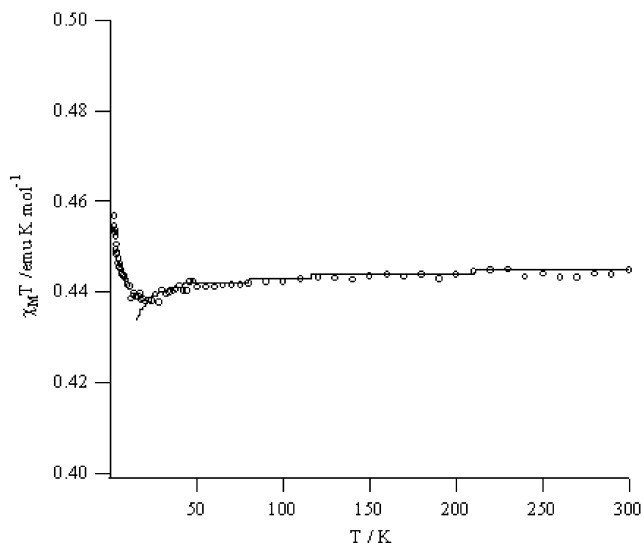
Fig. 6. Temperature dependence of $\chi_M T$ for compound **1**. The circles correspond to the experimental data, the simulation is depicted as a line.

Acknowledgments

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