

Alcoholysis/hydrolysis of 1,1'-carbonyldiimidazole as a means of preparing unprecedented, imidazole-containing one-dimensional coordination polymers of copper(II)[†]

Theocharis C. Stamatatos,^{a,b} Spyros P. Perlepes,^a Catherine P. Raptopoulou,^c Aris Terzis,^c Costas S. Patrickios,^b Anastasios J. Tasiopoulos^b and Athanassios K. Boudalis^{*c}

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The use of 1,1'-carbonyldiimidazole, (im)₂CO, for the synthesis of imidazolate (im⁻) and/or imidazole (Him)-containing copper(II) coordination polymers is described. The [Cu₂(O₂CMe)₄(H₂O)₂]/(im)₂CO reaction system in EtOH yields the new polymeric species [Cu(O₂CMe)(im)(Him)(EtOH)]_n (**1**) and the known compound [Cu(im)₂]_n (**2**), depending on the reaction conditions. A mechanism for the alcoholysis/hydrolysis of (im)₂CO is proposed. Complex **1** comprises neutral, zigzag chains with the η¹:η¹:μ im⁻ ligand bridging two neighbouring Cu^{II} atoms. Each square pyramidal metal centre is coordinated to two imidazolate nitrogen atoms, the pyridine-type nitrogen atom of the terminal imidazole ligand, one acetate oxygen atom and the ethanol oxygen atom. The dc magnetic susceptibility data for **1** have been analysed according to the Bonner-Fisher model for an equally spaced $S = 1/2$ chain, revealing moderate antiferromagnetic Cu^{II}...Cu^{II} exchange interactions ($J = -33.5 \text{ cm}^{-1}$ using the $H = -2J \sum_i \hat{S}_i \hat{S}_{i+1}$ spin Hamiltonian). The reaction system Cu(NO₃)₂·3H₂O/(im)₂CO in EtOH leading to the preparation of known *trans*-[Cu(NO₃)₂(Him)₄] (**3**) is also described. With terephthalate(−2) (tp²⁻), instead of MeCO₂⁻, in MeOH/H₂O the product is the new, 1D linear coordination polymer [Cu(tp)(Him)₂(H₂O)]_n·2nH₂O (**4**·2nH₂O). Adjacent square pyramidal Cu^{II} atoms are singly bridged by the bis-monodentate tp²⁻ ligand, while two monodentate Him groups and one H₂O molecule complete five-coordination at each metal centre. The chains of **1** and **4**·2nH₂O form interesting, hydrogen-bonded 3D networks. The combined work demonstrates the usefulness of (im)₂CO in the preparation of interesting Cu^{II} coordination polymers which can not be obtained by the use of Him.

Introduction

The utilisation of organic polymers, mainly composed of the elements C, H, O, N and—to a lesser extent—some neighbouring main group elements such as B, Si, P and S, in the 1960s transformed the way in which we live. In the field of polymers, the metallic elements, which comprise more than half of the elements in the Periodic Table, had comparatively less to contribute until the early 1990s.¹ However, this situation has changed in the last 15 years; the reason is that metal ions have attractive features for new generations of metalloorganic polymers, which are also known² as coordination polymers,^{3a} metal-organic coordination networks, metal-organic frameworks^{3b} or organic-inorganic hybrid coordination polymers. To date, scientists have realised various applications of coordination polymers in catalysis, electrical conductivity, luminescence, magnetism, non-linear optics, molecular electronics, sensing, drug delivery and zeolitic behaviour.^{2,4,5}

The ultimate goal is the transformation of few coordination polymers to functional molecular materials. Coordination polymers are also significant from a structural chemistry perspective with new, intriguing molecular topologies being discovered, as well as providing numerous examples of interesting phenomena such as the interpenetration of networks.⁶

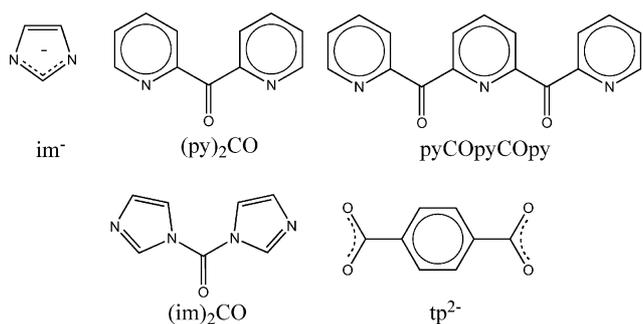
However, the factors influencing the synthesis of coordination polymers are still not completely understood and inorganic chemists are always looking for new methods that can lead to predictable products. The two main trends in the field are the 'synthesis by design' and the 'non-programmed assembly'. The former involves the use of rigid, often complicated organic ligands that will 'force' or 'drive' the precipitation of the desired product. The latter approach involves the use of more flexible ligands and lacks control over the final product, but it has proven to be successful in the synthesis of polymeric compounds with interesting structures and properties.^{2,4}

The π-excessive and strong σ-donor ligand imidazole (Him) has played a formative role in the development of coordination chemistry.⁷ The imidazolate anion (im⁻, Scheme 1), obtained by deprotonation of Him, is capable of acting as a bidentate bridging ligand. The 1,3-arrangement of the N atoms imposes geometrical constraints such that only one imidazolate bridge is possible between two metal centres. Accordingly,

^aDepartment of Chemistry, University of Patras, 265 04, Patras, Greece

^bDepartment of Chemistry, University of Cyprus, 264 43, Nicosia, Cyprus
^cInstitute of Materials Science, NCSR "Demokritos", 153 10, Aghia Paraskevi Attikis, Greece. E-mail: tbou@ims.demokritos.gr; Tel: +30 210 6503346

[†]CCDC reference numbers 715757 for **1** and 715758 for **4**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b900716d

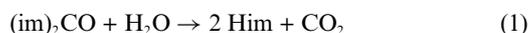


Scheme 1 Structural formulae and abbreviations of some of the ligands discussed in the text.

imidazolate-bridged transition metal complexes show a high degree of linearity. Restricting discussion to copper(II), only few imidazolate-bridged Cu^{II} coordination polymers are known.⁸ The usual methods for the preparation of such complexes involve direct reactions of Cu^{II} sources and imidazole in the absence or presence of ancillary ligands.

Our group has had a strong interest over many years in the coordination chemistry of ligands of the general types X-CO-X and X-CO-X-CO-X. Examples of two thoroughly studied such ligands are di-2-pyridyl ketone,^{9,10} (py)₂CO, and 2,6-di-(2-pyridylcarbonyl)pyridine,¹¹ (py)CO(py)CO(py) (Scheme 1), which have led to a multitude of polynuclear complexes (clusters) with a variety of metal ions and nuclearities reaching 26, some of them with interesting spin topologies and exciting magnetic properties. The particular interest on these two ligands stems from the reactivity potential of the carbonyl function(s) which can undergo metal ion-assisted hydrolysis or alcoholysis and subsequent deprotonation of the hydroxyl group(s). The deprotonated forms are coordinatively very versatile and can adopt a variety of bridging modes. With this previous experience in mind we sought to modify the possibilities provided by (py)₂CO by studying the coordination chemistry of X-CO-X molecules that would favour the isolation of coordination polymers. The first ligand of our choice was 1,1'-carbonyldiimidazole, (im)₂CO (Scheme 1), a well known reagent in organic synthesis.¹²

The free ligand exhibits very high reactivity toward nucleophilic reagents, because of the electron attraction exerted from both sides on the carbonyl group by the heterocycle. For example, H₂O hydrolyzes (im)₂CO at room temperature within seconds, with vigorous evolution of CO₂ as shown in eqn (1).¹³



(im)₂CO also reacts with alcohols forming diesters of carbonic acid or imidazole-*N*-carboxylic esters and yielding free imidazole.¹³ Thus, at the outset of our efforts we were aware that (im)₂CO could not be incorporated in metal complexes in aqueous or alcoholic reaction media. However, we hoped that such reactions would likely give polymeric metal complexes containing the bridging imidazolate(-1) ligand (im⁻), different from those obtained with the use of Him as starting material. This has, indeed, turned out to be the case. We herein report the initial results of our approach in copper(II) chemistry, namely the use of 1,1'-carbonyldiimidazole, (im)₂CO, as a reagent for synthesis of interesting Cu^{II} complexes containing im⁻ and/or Him ligands.

Experimental

All manipulations were performed under aerobic conditions using reagents and solvents as received.

[Cu(O₂CMe)(im)(Him)(EtOH)]_n (1) and [Cu(im)₂]_n (2) in a mixture

A green-blue solution of [Cu₂(O₂CMe)₄(H₂O)₂] (0.200 g, 0.50 mmol) in warm EtOH (15 mL) was added dropwise to a colourless solution of (im)₂CO (0.195 g, 1.20 mmol) in the same solvent (10 mL). The resulting deep blue solution was refluxed for 2 h, during which time a small amount of a purple solid (2) precipitated. An intense effervescence was observed. The obtained material was filtered off and dried in *vacuo* over silica gel. The filtrate from this procedure was layered with n-hexane (50 mL). After 5 days, blue crystals of 1 were collected by filtration, washed with cold EtOH (2 × 2 mL) and Et₂O (2 × 5 mL), and dried in *vacuo* over silica gel; the yield was ~55%. Data for 1: Anal. Calc. for C₁₀H₁₆CuN₄O₃: C, 39.53; H, 5.32; N, 18.44. Found: C, 39.34; H, 5.41; N, 18.35%. IR (KBr, cm⁻¹): 3410sb, 3145mb, 1583vs, 1556s, 1471s, 1412s, 1328m, 1276w, 1255m, 1228m, 1174m, 1140m, 1086vs, 1068s, 1047m, 945m, 828m, 755m, 654s, 618m. Data for 2: Anal. Calc. for C₆H₆CuN₄: C, 36.45; H, 3.07; N, 28.35. Found: C, 36.18; H, 3.11; N, 28.29%. IR (KBr, cm⁻¹): 2917w, 1598s, 1535m, 1464m, 1407m, 1382w, 1309m, 1234m, 1168w, 1085vs, 945m, 834m, 808m, 755s, 670s, 615m.

[Cu(O₂CMe)(im)(Him)(EtOH)]_n (1)

To a stirred green-blue solution of [Cu₂(O₂CMe)₄(H₂O)₂] (0.200 g, 0.50 mmol) in EtOH (25 mL) was added a solution of (im)₂CO (0.243 g, 1.50 mmol) in the same solvent (10 mL). An intense effervescence was observed. The resulting deep blue solution was refluxed for 15 min and stored in the refrigerator (4–5 °C) for one week. Blue crystals of 1 formed, which were collected by filtration, washed with Et₂O (2 × 5 mL), and dried in *vacuo* over silica gel; the yield was ~40%. The identity of the product was confirmed by elemental analysis (Calc. for C₁₀H₁₆CuN₄O₃: C, 39.53; H, 5.32; N, 18.44. Found: C, 39.60; H, 5.21; N, 18.25%), and IR spectroscopic comparison with the blue crystals from the above mentioned procedure that gave a mixture of 1 and 2.

[Cu(im)₂]_n (2)

To a stirred green-blue solution of [Cu₂(O₂CMe)₄(H₂O)₂] (0.200 g, 0.50 mmol) in EtOH (25 mL) was added solid (im)₂CO (0.130 g, 0.80 mmol). The solid dissolved immediately followed by a colour change to purple and an effervescence. The solution was stirred for a further 5 min and left undisturbed in a closed flask. After 2 days, X-ray quality purple crystals of the product were collected by filtration and dried in air; the yield was ~35%. The identity of this material was confirmed by comparison of its unit cell parameters with those available in the literature,^{14a} and elemental analysis (Calc. for C₆H₆CuN₄: C, 36.45; H, 3.07; N, 28.35. Found: C, 36.83; H, 3.02; N, 28.55%). The IR spectrum of the crystals was identical to that of the purple solid isolated from the above mentioned procedure that resulted in the mixture of 1 and 2.

trans-[Cu(NO₃)₂(Him)₄] (3)

Method A. Treatment of a pale blue solution of Cu(NO₃)₂·3H₂O (0.121 g, 0.50 mmol) in EtOH (20 mL) with solid (im)₂CO (0.162 g, 1.00 mmol) resulted in a blue solution which was stirred for a further 30 min without any noticeable colour change. An effervescence was noticed during stirring. The resulting solution was filtered and the filtrate layered with *n*-hexane (40 mL). Slow mixing gave deep purple crystals of the product which were collected by filtration, washed with cold Et₂O (2 × 5 mL) and dried in *vacuo* over silica gel; the yield was ~85%. Determination of the unit cell parameters revealed that this compound is the known complex *trans*-[Cu(NO₃)₂(Him)₄].^{14b} Anal. Calc. for C₁₂H₁₆CuN₁₀O₆: C, 31.34; H, 3.51; N, 30.46. Found: C, 31.24; H, 3.57; N, 30.36%. IR (KBr, cm⁻¹): 3135s, 1753w, 1637m, 1538m, 1495m, 1451m, 1384vs, 1315m, 1259m, 1170m, 1134m, 1098s, 1068vs, 943m, 923w, 852m, 824m, 749s, 610s.

Method B. Solid Cu(NO₃)₂·3H₂O (0.121 g, 0.50 mmol) and (im)₂CO (0.162 g, 1.00 mmol) were manually grinded in a Petri dish for 5 min, during which time a vigorous effervescence occurred. The resulting blue slurry was extracted with the minimum volume of EtOH (6 mL) giving a deep blue solution. This solution was allowed to slowly evaporate at room temperature. Deep purple crystals of **3** formed over 2 days. The crystals were collected by filtration, washed with cold Et₂O (2 × 5 mL) and dried in *vacuo* over silica gel. The yield was low (~30%) but the reaction is reproducible. The identity of this material was confirmed by elemental analysis (Calc. for C₁₂H₁₆CuN₁₀O₆: C, 31.34; H, 3.51; N, 30.46. Found: C, 31.60; H, 3.40; N, 30.00%), and IR spectroscopic comparison with material from method A.

[Cu(tp)(Him)₂(H₂O)]_{*n*}·2*n*H₂O (4·2*n*H₂O)

Method A. To a stirred, colourless solution of H₂tp (0.083 g, 0.50 mmol) and LiOH·H₂O (0.042 g, 1.00 mmol) in H₂O (10 mL) was added a blue solution of Cu(NO₃)₂·3H₂O (0.121 g, 0.50 mmol) and (im)₂CO (0.162 g, 1.00 mmol) in MeOH (15 mL). Effervescence was observed. The resulting green-blue slurry was stirred for a further 10 min, the insoluble material was filtered and the filtrate layered with Me₂CO (50 mL). After 2 days, blue crystals of 4·2*n*H₂O formed, which were collected by filtration, washed with cold Me₂CO (2 × 5 mL) and Et₂O (3 × 5 mL), and dried in *vacuo* over silica gel; the yield was ~60%. The dried solid analysed as 4·*n*H₂O. Anal. Calc. for C₁₄H₁₆CuN₄O₆: C, 42.05; H, 4.04; N, 14.01. Found: C, 41.94; H, 4.12; N, 13.96%. IR (KBr, cm⁻¹): 3419s, ~3200mb, 2930w, 1618s, 1540m, 1501m, 1471m, 1397s, 1367s, 1230m, 1069s, 947m, 855m, 818m, 739s, 658s, 615m, 566m.

Method B. To a stirred, colourless solution of H₂tp (0.083 g, 0.50 mmol) and LiOH·H₂O (0.042 g, 1.00 mmol) in H₂O (10 mL) was added a blue solution of complex **3** (0.230 g, 0.50 mmol) in the same solvent (10 mL). The resulting green-blue solution was stirred for a further 10 min at room temperature and layered with Me₂CO (40 mL). After few days, blue crystals of 4·2*n*H₂O were collected by filtration, washed with cold Me₂CO (2 × 3 mL) and Et₂O (2 × 3 mL), and dried in *vacuo* over silica gel; the yield was 35%. The identity of the product was confirmed by elemental analysis (the material analysed satisfactorily as 4·*n*H₂O; Calc. for

Table 1 Crystallographic data for complexes **1** and 4·2*n*H₂O

	1	4·2 <i>n</i> H ₂ O
Formula ^a	C ₁₀ H ₁₆ CuN ₄ O ₃	C ₁₄ H ₁₆ CuN ₄ O ₇
<i>M</i> /g mol ⁻¹	303.81	417.86
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	11.686(5)	13.815(8)
<i>b</i> /Å	14.239(5)	5.931(3)
<i>c</i> /Å	8.467(3)	22.02(1)
<i>β</i> /°	108.27(2)	101.81(2)
<i>V</i> /Å ³	1338.0(9)	1766(2)
<i>Z</i>	4	4
<i>F</i> (000)	628	860
<i>T</i> /K	298	298
<i>λ</i> /Å	1.54180 ^b	1.54180 ^b
<i>ρ</i> _c /g cm ⁻³	1.508	1.572
<i>μ</i> /mm ⁻¹	2.387 ^b	2.165 ^b
Meas./indep. refl. (<i>R</i> _{int})	2162/2016 (0.0315)	1317/1282 (0.1081)
Obs. refl. [<i>I</i> > 2σ(<i>I</i>)]	1822	1175
<i>wR</i> 2 ^c	0.1426	0.1281
<i>R</i> 1 ^d	0.0479	0.0457
Goodness of fit on <i>F</i> ²	1.069	1.148
Δ <i>ρ</i> _{max, min} /e Å ⁻³	0.672/−0.637	0.563/−0.804

^a Including solvate molecules. ^b Cu Kα radiation, graphite monochromator. ^c *wR*2 = {∑[*w*(*F*_o² − *F*_c²)²]/∑[*w*(*F*_o²)²]}^{1/2}. ^d *R*1 = ∑|*F*_o − |*F*_c||/∑|*F*_o|.

C₁₄H₁₆CuN₄O₆: C, 42.05; H, 4.04; N, 14.01. Found: C, 42.20; H, 4.00; N, 13.82%), and IR spectroscopic comparison with authentic material from method A.

X-Ray crystallography

Crystallographic data together with refinement details for the new complexes reported in this work are summarized in Table 1. The selected crystals of **1** (0.14 × 0.20 × 0.40 mm) and 4·2*n*H₂O (0.05 × 0.15 × 0.30 mm) were mounted in capillary, while those of **3** (0.08 × 0.18 × 0.60 mm) were mounted in air. Data were collected using a Crystal Logic Dual Goniometer diffractometer equipped with a graphite monochromator utilising Mo Kα radiation (for complex **3**) and on a P2₁ Nicolet diffractometer upgraded by Crystal Logic using graphite monochromated Cu Kα radiation (for complexes **1** and 4·2*n*H₂O). Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections in the range 22 < 2θ < 54° (for complexes **1** and 4·2*n*H₂O) and 11 < 2θ < 23° (for complex **3**). Intensity data were recorded using a θ-2θ scan to a max 2θ value of 122 (**1**) and 118° (4·2*n*H₂O). Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz and polarization corrections were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXS-86¹⁵ and refined by full-matrix least-squares on *F*² with SHELXL-97.¹⁶ For **1** all H atoms were introduced at calculated positions as riding on bonded atoms; for 4·2*n*H₂O all H atoms were located by difference maps and refined isotropically. All non-hydrogen atoms of complexes **1** and 4·2*n*H₂O were refined anisotropically.

Physical studies

Elemental analyses (C, H, N) were performed by the in-house facilities of the Chemistry Department at the University of Cyprus

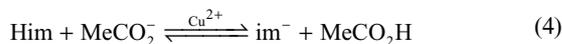
using an Euro Vector EA elemental analyzer. Infrared spectra were recorded in the solid state (KBr pellets) on a Perkin Elmer PC 16 FTIR spectrometer in the 4000–500 cm⁻¹ range. Magnetic measurements of **1** were carried out on freshly isolated and dried samples on a Quantum Design MPMS-5.5 SQUID susceptometer under a field of 0.1 T, and between the 5–300 K temperature range. Data were corrected with standard procedures for the contribution of the sample holder and diamagnetism of the sample. The magnetic susceptibility has been computed by an analytical expression. Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT.¹⁷ The error factor *R* is defined as $R = \sum[(\chi_{\text{exp}} - \chi_{\text{calc}})^2 / N\chi_{\text{exp}}^2]$, where *N* is the number of experimental points.

Results and discussion

Syntheses and IR spectra

The original aim of this synthetic program was to explore the use of (im)₂CO for the assembly of coordination polymers of 3d-metals possessing bridging imidazolate (im⁻) ligands. One of our routes takes advantage of the fact that the reactions between metal carboxylates and (im)₂CO in alcohols or/and H₂O are excellent springboards to a variety of such products. Obviously the produced Him (see eqn (1)) can be deprotonated by the RCO₂⁻ groups in the presence of metal ions and we anticipated new types of polymeric Mⁿ⁺/im⁻/RCO₂⁻ species as long as the RCO₂⁻ to Him ratio was high enough to leave an amount of nonprotonated carboxylates in the reaction mixture, given the fact that both im⁻ and RCO₂⁻ can potentially adopt bridging modes. This idea proved to be both successful and unsuccessful.

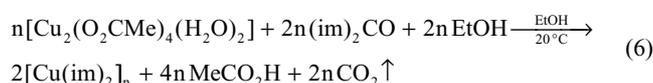
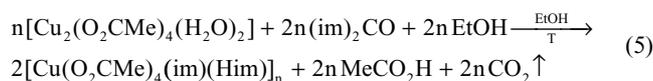
Our initial efforts involved the reaction of [Cu₂(O₂CMe)₄(H₂O)₂] with 2.4 equivs of (im)₂CO, *i.e.*, a potential Cu^{II}/MeCO₂⁻/Him reaction ratio of 1:2:2.4, in EtOH under reflux. A purple, polycrystalline material, repeatedly analysed as Cu(im)₂ and blue crystals, crystallographically characterized as the 1D polymeric compound [Cu(O₂CMe)(im)(Him)(EtOH)]_{*n*} (**1**), were isolated. In eqn (2)–(4) we propose a simplistic reaction scheme that may explain the observed (im)₂CO to im⁻ transformation. A detailed mechanistic perspective is beyond our intention.



According to the above equations, the first step of this transformation involves the ethanolysis of (im)₂CO to the corresponding imidazole-*N*-carboxylic ethyl ester, followed by the hydrolysis (from the water present in the solvent and in the starting Cu^{II} material) of the ester group to form a second equivalent of Him. The third step involves the Cu^{II}-mediated deprotonation of Him by the strongly basic acetate. It is difficult to decide if the step represented by eqn (2) is Cu^{II}-assisted. Coordination of the oxygen atom of the carbonyl group in solution is likely to enhance the reactivity of that group.¹⁸ The metal centre polarises the carbonyl group and EtOH can attack the carbonyl carbon to generate the tetrahedral intermediate before the ester formation. It is noteworthy that a similar transformation of (im)₂CO to

im⁻ has been reported by Ghosh and co-workers.^{19a} The 1:3 reaction of Cu(ClO₄)₂·6H₂O and (im)₂CO in MeOH-H₂O yielded complex [Cu₃(ClO₄)₄(im)₂(Him)₈]_{*n*} containing both imidazolate and perchlorate bridges; the authors avoided mechanistic discussions. However, this complex had been prepared and structurally characterized before from the use of Him as starting material.^{19b}

With the identities of the purple powder and blue crystals established by elemental analysis and single-crystal, X-ray crystallography, respectively, convenient syntheses of pure materials were sought under alternative reaction conditions. In both compounds, the Cu^{II} to imidazole molar ratio is the same, *i.e.*, 1:2. However, the purple material seemed to contain only anionic imidazolate ligands. Thus, attempts to obtain pure **1** and the purple powder were made by decreasing and increasing, respectively, the MeCO₂⁻ to (im)₂CO reaction ratio. Using the modified MeCO₂⁻/(im)₂CO ratios of 2:1.5 (~1.3) and 2:0.8 (2.5), we isolated **1** and the purple powder, respectively. Note that the MeCO₂⁻ to (im)₂CO ratio is ~1.7 in the experiments that lead to the mixture of products (see Experimental). We were lucky enough to isolate X-ray quality crystals of the purple material. Examination of the unit cell parameters revealed that the purple compound is the known complex¹⁴ *catena*-bis(μ-imidazolate-*N,N'*)copper(II), [Cu(im)₂]_{*n*} (**2**). The formation of the two coordination polymers is summarized in eqn (5) and (6). In both of these balanced equations, the MeCO₂⁻ to (im)₂CO ratio is the same, *i.e.*, 2.0. The excess of acetates in the preparation of pure **2** shifts the equilibrium (4) to the right and this ensures the presence of all the amount of imidazole in its deprotonated form. The excess of (im)₂CO (and hence of Him derived from the decomposition shown in eqn (1)) in the preparation of pure **1** seems necessary for the presence of a considerable concentration of neutral imidazole in the reaction solution.

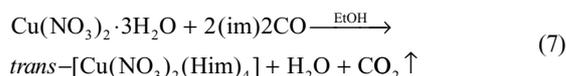


The temperature is another synthetic parameter in the [Cu₂(O₂CMe)₄(H₂O)₂]/(im)₂CO reaction system. We have observed that the isolation of **1** is favoured if the reaction solution is refluxed before the crystallisation procedure. For example, if the reaction mixture that leads to pure **2** undergoes reflux, then the product is contaminated with various amounts of **1** (analytical and IR evidence). Thus, the reactions that give pure **1** and **2** take place under reflux and at room temperature, respectively.

The presence of both EtOH and Him ligands in **1** is manifested by two broad IR bands at ~3400 and ~3150 cm⁻¹, assigned to ν(OH)_{EtOH}²⁰ and ν(NH)_{Him},^{19a} respectively. The spectra of **1** and **2** do not exhibit a band in the region for the carbonyl stretching band as expected, with the bands at 1556 (**1**) and 1598 (**2**) cm⁻¹ assigned to ν(C=N). The strong bands at 1583 and 1412 cm⁻¹ in the spectrum of **1** are assigned to ν_{as}(CO₂) and ν_s(CO₂), respectively.²¹

Having been encouraged by the above mentioned experiments that (im)₂CO in EtOH was indeed capable of giving clean reactions and polymeric species containing im⁻ ligands, our attention now turned to the preparation of simple mononuclear complexes, available by other methods, containing exclusively neutral Him

ligands. Preliminary screening showed clean reactions could be obtained by using a variety of weakly basic inorganic anions, *e.g.*, Cl⁻, Br⁻, NO₃⁻ *etc.* in both MeOH and EtOH, but the NO₃⁻/EtOH combination was found to yield the most crystalline product. Thus, treatment of a Cu(NO₃)₂·3H₂O solution in EtOH with two equivs of (im)₂CO yielded a homogeneous, blue solution, from which the known complex^{14b} *trans*-[Cu(NO₃)₂(Him)₄] (**3**) crystallised. The formation of **3** is summarised in eqn (7).

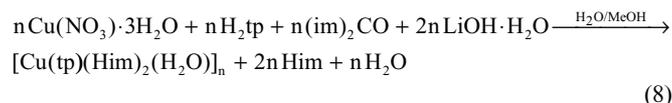


The high yield of the preparation (>85% based on the available Cu^{II}) strengthens our view that the decomposition of (im)₂CO in EtOH occurs in two steps, see eqn (2) and (3), producing two equivalents of Him per (im)₂CO. This is in accordance with the observed effervescence during the reaction. This reaction does not seem particularly alcohol dependent; the compound was obtained cleanly in isolated yields of 40–70% from MeOH and PrⁿOH. These yields are not optimized; no attempts to obtain more product from the coloured mother liquors were made. Complex **3** can also be prepared by a solid state-type reaction of Cu(NO₃)₂·3H₂O and (im)₂CO in a 1:2 molar ratio and subsequent isolation of the well-formed deep purple crystals from EtOH (method B in Experimental).

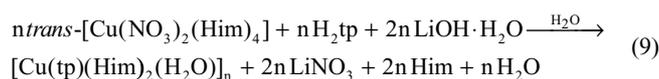
The bands at 1451 and 1315 cm⁻¹ in the IR spectrum of **3** are assigned²² to the ν₃(B₂) and ν₁(A₁) (under C_{2v} symmetry), respectively, of the nitrate ligands; their separation is small (136 cm⁻¹) in accordance with the crystallographically established^{14b} monodentate character of the two nitrate groups.²² The two bands appear at the same wavenumbers in the mull (nujol, hexachlorobutadiene) spectra of **3**.

Having obtained and identified complex **1**, another question addressed was in what manner changes in the carboxylate anion might affect the product identity. Since **1** contains a bridging im⁻ ligand and a terminal MeCO₂⁻ group, we were interested in preparing polymeric Cu^{II} species possessing both imidazolite and carboxylate groups as bridging ligands. An obvious choice was a dicarboxylate ligand. Preliminary experiments were highly encouraging using the benzene-1,4-dicarboxylate(-2) (terephthalate; tp²⁻, Scheme 1) ligand. The tp²⁻ ion is a versatile ligand as exemplified by the formation of polymeric structures.²³ Terephthalato(-2)-bridged complexes have been actively studied to elucidate the limiting distance of magnetic exchange between paramagnetic metal centres. The tp²⁻ bridges typically give rise to M···M separations of ~11 Å, which generally lead to weak antiferromagnetic interactions for M = Mn^{II}, Co^{II}, Ni^{II} and Cu^{II}.²⁴ The 1:1:2 reaction between Cu(NO₃)₂·3H₂O, H₂tp and (im)₂CO in H₂O/MeOH in the presence of two equivs of OH⁻ produced the 1D coordination polymer [Cu(tp)(Him)₂(H₂O)]_n·2nH₂O (**4**·2nH₂O). The preparation of **4** is summarized in eqn (8). Although we were rather disappointed to see (*vide infra*) that the complex contains neutral, terminal imidazole ligands, we proceeded with its characterization because it is a rare example of a Cu^{II} terephthalate(-2) complex containing monodentate ancillary ligands. The excess (im)₂CO used in the preparation of **4** is beneficial to the yield; when the stoichiometric amount (Cu^{II}:H₂tp:(im)₂CO:OH⁻ = 1:1:1:2) was used, the yield was lower than 40%. In an attempt to prepare a Cu^{II} polymer with both tp²⁻ and im⁻ ligands, we explored reaction

systems with Cu^{II}:H₂tp:(im)₂CO:OH⁻ ratios of 1:1:1:3 or 4 (the cations of the bases were Me₃N⁺, Et₄N⁺ and Bu₄ⁿN⁺ to favour formation of anionic polymeric species). However, these led to product **4** in low (<20%) yields contaminated with amorphous Cu^{II} hydroxo species. These combined results suggest complex **4** to be the thermodynamically favoured product under these reaction conditions. This conclusion is further supported by the observation that use of >2 equivs of (im)₂CO and <1 equivs of H₂tp in the reactions (to see what type of compound might result if the Cu^{II} to tp²⁻ ratio in the product was 2:1), led only to the same complex **4** being isolated.



Complex **4** can also be prepared by the 1:1 reaction between the pre-isolated complex **3** and tp²⁻ in H₂O but in a lower yield (~35%); the reaction is summarized in eqn (9).



The strong bands at 1618 and 1397 cm⁻¹ in the IR spectrum of **4** are assigned²⁴ to ν_{as}(CO₂) and ν_s(CO₂), respectively. The difference Δ (221 cm⁻¹) suggests the presence of monodentate carboxylate groups^{21,24} in agreement with the structure of the complex (*vide infra*).

Description of structures

Partially labeled representations of complexes **1** and **4**·2nH₂O are shown in Fig. 1–4. Selected interatomic distances and angles are listed in Tables 2 and 3. Hydrogen bonding details for complex **4**·2nH₂O are given in Table 4.

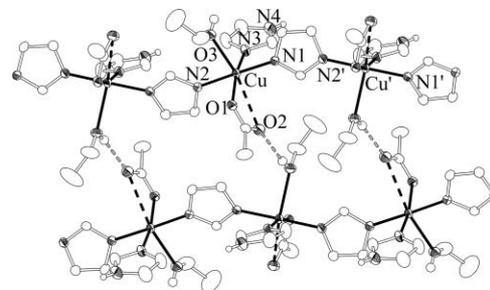


Fig. 1 Partially labelled plot of a hydrogen-bonded pair of portions of 1D chains in **1**. For clarity only H(O3) and H(N4) hydrogen atoms are shown. Weak Cu···O(2) interactions are shown as black dashed lines, and H(O3)···O(2) hydrogen bonds are shown as grey dashed lines. Primed and unprimed atoms are symmetry-related ($\prime = 0.5 + x, 1.5 - y, 0.5 - z$).

Complex **1** (Fig. 1 and 2) crystallises in the monoclinic space group $P2_1/n$. The complex is a 1D coordination polymer comprising neutral, zigzag [Cu(O₂CMe)(im)(Him)(EtOH)]_n chains. The η¹:η¹:μ im⁻ ligand bridges two neighbouring Cu^{II} atoms, thus promoting the formation of the chain. The Cu^{II} centre is coordinated to two nitrogen atoms, N(1) and N(2), of the bridging imidazolite anion in a *trans* manner, one nitrogen atom, N(3), of the terminal Him ligand, one oxygen atom, O(1), of the

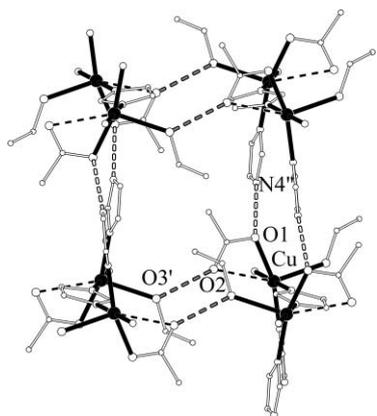


Fig. 2 Partially labelled plot showing the packing of the chains in **1** through hydrogen bonds.

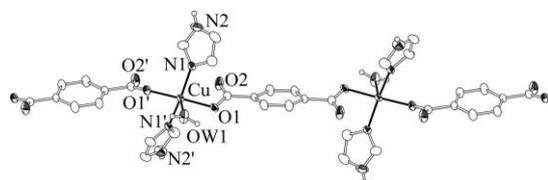


Fig. 3 Partially labelled plot of a portion of the 1D chain in $4 \cdot 2n\text{H}_2\text{O}$. For clarity only H(N1) and H(N2) hydrogen atoms are shown. Primed and unprimed atoms are symmetry-related ($' = 0.5 + x, 1.5 - y, 0.5 + z$).

monodentate MeCO_2^- group and the oxygen atom, O(3), of the terminal EtOH molecule.

The metal coordination geometry is well described as distorted square pyramidal with the coordinated EtOH molecule occupying the apical position. Analysis of the shape-determining angles using the approach of Reedijk, Addison and co-workers²⁵ yields a trigonality index, τ , value of 0.23 for Cu ($\tau = 0$ and 1 for perfect *sp* and *tbp* geometries, respectively). Cu lies 0.142(1) Å above the N(1), N(2), N(3), O(1) least-squares plane (max deviation

Table 2 Selected interatomic distances (Å) and angles (°) for complex **1**^a

Cu–O(1)	2.039(2)
Cu–O(3)	2.385(2)
Cu–N(1)	1.989(3)
Cu–N(2)	1.984(3)
Cu–N(3)	2.030(3)
Cu...Cu'	6.047(8)
Cu...O(2)	2.764(2)
O(1)–Cu–O(3)	99.0(1)
O(1)–Cu–N(1)	90.8(1)
O(1)–Cu–N(2)	87.6(1)
O(1)–Cu–N(3)	164.7(1)
O(3)–Cu–N(1)	92.4(1)
O(3)–Cu–N(2)	88.4(1)
O(3)–Cu–N(3)	96.2(1)
N(1)–Cu–N(2)	178.4(1)
N(1)–Cu–N(3)	89.8(1)
N(2)–Cu–N(3)	91.5(1)

^a Symmetry code ($'$): $0.5+x, 1.5-y, 0.5+z$.

Table 3 Selected interatomic distances (Å) and angles (°) for complex **4·2nH₂O**^a

Cu–O(1)	1.967(3)
Cu–O(1')	1.967(3)
Cu–OW(1)	2.278(4)
Cu–N(1)	1.982(3)
Cu–N(1')	1.982(3)
Cu...Cu#	11.025(3)
O(1)–Cu–O(1')	176.3(1)
O(1)–Cu–OW(1)	88.1(7)
O(1)–Cu–N(1)	89.6(1)
O(1)–Cu–N(1')	90.9(1)
OW(1)–Cu–N(1)	97.8(9)
N(1)–Cu–N(1')	164.4(2)

^a Symmetry code ($'$): $-x, y, -z + 1/2$; ($\#$): $x, -y, z + 1/2$.

0.129(1) Å by N(2)) towards O(3). As expected, the axial Cu–O(3) bond is the longest (2.385(3) Å). The *trans* coordination angles are 164.7(1) (O(1)–Cu–N(3)) and 178.4(1)° (N(1)–Cu–N(2)). The

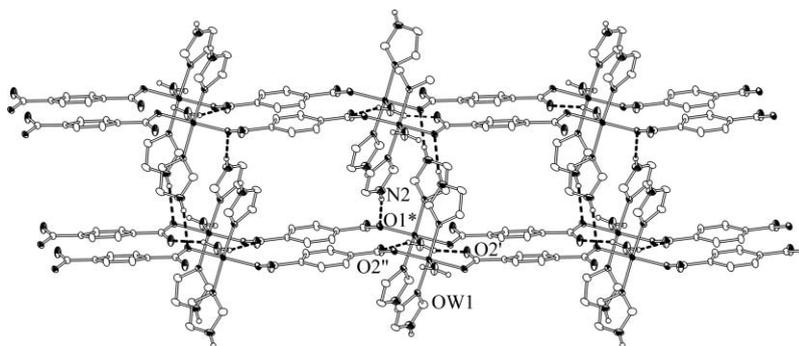


Fig. 4 Hydrogen bonding between the chains in $4 \cdot 2n\text{H}_2\text{O}$. Primes, double primes and asterisks correspond to the symmetry operations described in Table 4. The lattice H_2O molecules are not shown.

Table 4 Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for complex $4 \cdot 2n\text{H}_2\text{O}$ (A = Acceptor; D = Donor)

H Bond	D...A	H...A	D–H...A	Symmetry operator
OW1–(OW1)...O2'	2.799(3)	2.006(3)	162.7(1)	$' = x, 1 + y, z$
OW1–(OW1)...O2''	2.799(3)	2.006(3)	162.7(1)	$'' = -x, 1 + y, 0.5 - z$
N2–H(N2)...O1*	2.962(2)	2.082(2)	162.7(1)	$* = 0.5 + x, -0.5 + y, z$

carboxylate group of the MeCO_2^- ligand can be alternatively considered as asymmetric chelating ($\eta^1:\eta^1$) as evidenced by the Cu–O distances of 2.039(2) and 2.764(2) Å. Adopting this alternative description of the acetate coordination mode, the Cu coordination geometry may be described as very distorted octahedral with the weakly interacting O(2) atom occupying the second axial position at the metal; this view is emphasized in Fig. 1.

Within the imidazolate-bridged chains, the distance between adjacent Cu^{II} centres is 6.047(8) Å. There are two types of Cu–N bonds: the Cu–N(3) bond to the neutral imidazole is slightly elongated at a distance of 2.030(3) Å, whereas the two other bonds to the bridging imidazolate ligand are shorter (average distance 1.987(3) Å). The latter two Cu–N(im⁻) bond lengths are in the reported range of 1.9–2.0 Å for other imidazolate-bridged complexes containing square pyramidal Cu^{II} atoms.^{8a,26} The bridging im⁻ ring is planar. This ring is flattened with the C–N–C angles (104.8(3) and 104.8(3)°) smaller, and the N–C–N (113.4(8)°) and C–C–N (108.4(3) and 108.5(3)°) angles larger than 108°. This type of flattening is typical for bridging im⁻ ligands.²⁶

The 1D chains of **1** (Fig. 2) are hydrogen-bonded into 3D frameworks through $\text{O}_{\text{MeCO}_2^-} \cdots \text{H}(\text{O}_{\text{EtOH}})$ and $\text{O}_{\text{MeCO}_2^-} \cdots \text{H}(\text{N}_{\text{Him}})$ interactions. The dimensions are: $\text{O}(3') \cdots \text{O}(2)$ 2.735(3) Å, $\text{O}(3')\text{---H}(\text{O}3') \cdots \text{O}(2)$ 169.1(1)° (symmetry code: ' = 0.5 – x, –0.5 + y, 0.5 – z) and $\text{N}(4'') \cdots \text{O}(1)$ 2.828 Å, $\text{N}(4'')\text{---H}(\text{N}4'')\text{---O}(1)$ = 162.8(1)° (symmetry code: '' = 0.5 + x, 1.5 – y, –0.5 + z); the closest interchain Cu^{II}···Cu separations are 7.185 and 8.221 Å, respectively. Closer inspection of the structure reveals that the very weak bonding Cu^{II}···O(2) interaction (2.764(2) Å) may be due to the involvement of O(2) in the interchain hydrogen bond with the coordinated EtOH oxygen atom; this hydrogen bond separates further O(2) from Cu.

Complex **1** joins a small family of imidazolate-bridged Cu^{II} coordination polymers.^{8,14,19} It is only the third example of a polymeric Cu^{II} compound containing both Him and im⁻ ligands, the two previous examples being $[\text{CuCl}(\text{im})(\text{Him})_2]_n$ ^{8b} and $[\text{Cu}_3(\text{ClO}_4)_4(\text{im})_2(\text{Him})_8]_n$ ¹⁹; in the latter, however, the bridging of the trinuclear repeating units to form the chain is achieved by perchlorate groups.

Complex $4\cdot 2n\text{H}_2\text{O}$ (Fig. 3 and 4) crystallises in the monoclinic space group $C2/c$. Its structure consists of neutral $[\text{Cu}(\text{tp})(\text{Him})_2(\text{H}_2\text{O})]_n$ chains and lattice H_2O molecules. There is a crystallographic inversion centre which is located at the middle of the benzene ring of the tp^{2-} ligand. Each chain consists of a linear array of Cu^{II} atoms parallel to the c axis. Adjacent metal ions are singly bridged by one bis-monodentate $\eta^1:\eta^1:\mu$ tp^{2-} ligand, coordinated in a monodentate fashion through each of its carboxylate groups. Two monodentate Him ligands and the H_2O molecule complete five-coordination at each metal centre.

The coordination geometry about the Cu^{II} centre is well described as square pyramidal ($\tau = 0.20$) with the aquo ligand occupying the axial position. The basal plane is defined by atoms O(1) and O(1') from two tp^{2-} ligands, and the pyridine-type atoms N(1) and N(1') from two Him ligands. As expected, the Cu–OW(1) bond is the longest (2.278(4) Å). The copper(II)–oxygen (carboxylate) bond distance (1.967(3) Å) and the intrachain intermetallic separation (11.025(3) Å) are in the corresponding ranges reported for bis-monodentate tp^{2-} -bridged copper(II) complexes containing 5-coordinate metal ions.²⁴

The chains of $4\cdot 2n\text{H}_2\text{O}$ form a hydrogen-bonded 3D network (Fig. 4), through a group of interactions listed in Table 4. The interchain Cu^{II}···Cu separations are 5.931(3) Å along the b axis and 7.517(4) Å along the a axis. The packing of the polymeric chains generates microchannels parallel to the c axis. The resulting cavities are filled by the solvate H_2O molecules.

Complex $4\cdot 2n\text{H}_2\text{O}$ joins a small family of structurally characterized, tp^{2-} -bridged polymeric Cu^{II} complexes also containing monodentate,^{23,27} bidentate²⁸ or tridentate²⁹ terminal N -donors as ancillary ligands. Complex $4\cdot 2n\text{H}_2\text{O}$ is unique in the group of polymeric Cu^{II} complexes with monodentate N -donors because it has three monodentate ligands per metal centre; all the other complexes^{23,27} have two. From that group, only the 1D complex $[\text{Cu}(\text{tp})(\text{NH}_3)_2]_n$ ^{27a} is structurally related to **4** in that it also has a bis-monodentate bridging tp^{2-} ligand. However, the Cu^{II} coordination geometry in the ammine complex is square planar (and not square pyramidal as in **4**), a consequence of the presence of two ammine ligands per metal ion.

Magnetic susceptibility studies on complex 1

Due to the large Cu^{II}···Cu distances in complex **2** and the probably weak exchange couplings that may result, we focused on the magnetic study of complex **1**. Variable-temperature dc magnetic susceptibility studies were performed on a powdered sample of **1** in the 5.0–300 K range. Samples of **1** suffered from ageing effects and the magnetic properties of aged samples could not be interpreted by assuming a simple 1D Heisenberg chain. Magnetic measurements were therefore carried out on freshly prepared and dried samples.

The $\chi_M T$ product for **1** (Fig. 5) at 300 K is 0.35 cm³ mol⁻¹ K, slightly lower than the spin-only value of an isolated $S = 1/2$ ion (0.38 cm³ mol⁻¹ K, $g = 2.0$). This shows a continuous drop upon cooling, consistent with the interplay of antiferromagnetic interactions. The magnetic susceptibility (χ_M) shows a smooth increase upon cooling until a broad maximum around 55 K, dropping to a minimum at 26 K, before increasing upon further cooling. The whole behaviour is typical of dominant antiferromagnetic interactions, while the increase at low temperatures is indicative of a paramagnetic impurity.

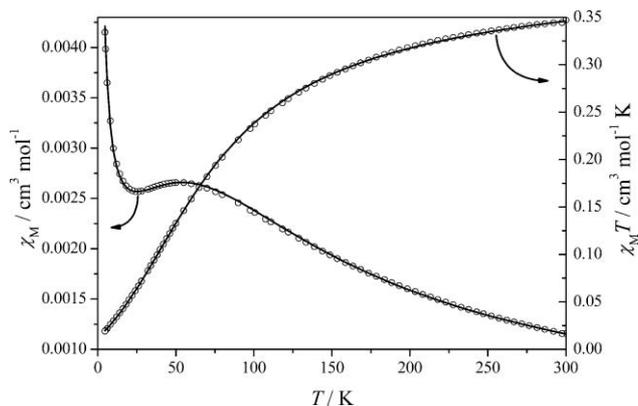


Fig. 5 χ_M vs. T and $\chi_M T$ vs. T data (open circles) and best-fit curves according to the above-mentioned model.

The magnetic properties were analyzed according to the Bonner-Fisher model,³⁰ for an equally spaced $S = 1/2$ chain. At a

first approximation interchain interactions were disregarded as too weak to be reliably accounted for by magnetic susceptibility measurements. The Hamiltonian considered was:

$$\hat{H} = -2J \sum_i \hat{S}_i \hat{S}_{i+1} \quad (10)$$

A rough estimate of *ca.* -30 cm^{-1} can be obtained for the exchange coupling based on the position of the χ_M vs. T curve maximum, according to the relation $kT_{\text{max}}/|J| = 1.282$, proposed by Bonner and Fisher ($-2JS_i S_j$ Hamiltonian formalism).

For the fitting of the data the empirical eqn (11) derived by Hall was employed.³¹

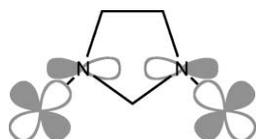
$$\chi_{\text{chain}} = \frac{Ng^2\beta^2}{kT} \left[\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \right] \quad (11)$$

with $A = 0.25$, $B = 0.14995$, $C = 0.30094$, $D = 1.9862$, $E = 0.68854$, $F = 6.0626$ and $x = |J|/kT$ for the above mentioned Hamiltonian formalism. The final expression used, accounts for a small fraction ρ of paramagnetic impurity ($S = 1/2$) obeying the Curie law:

$$\chi = (1-\rho)\chi_{\text{chain}} + \rho \frac{Ng^2\beta^2}{4kT} \quad (12)$$

According to this model, the best-fit parameters are: $J = -33.5 \text{ cm}^{-1}$, $g = 2.105$, $\rho = 2.8\%$ with $R = 2.3 \times 10^{-5}$. The high quality of the fit does not allow us to consider an interchain interaction without risk of overparametrizing the problem. The value of the derived J coupling falls within the range of 0 to -88 cm^{-1} previously reported^{26,32} for imidazolato-bridged copper(II) complexes, and can be characterized as moderate.

With one exception,³³ the magnetically coupled M–im–M(M') systems explored to date have displayed antiferromagnetic coupling, and the focus of study has been in establishing its magnitude and mechanism.^{7b, 26,33,34} Considering imidazolato-bridged copper systems, the interaction between the Cu^{II} centres can be explained in terms of a σ - and/or a π -exchange pathway. In general, there is agreement^{26,35} that the π orbitals of the im⁻ ligand are not involved in the coupling. Since the magnetic orbitals are σ antibonding for square planar and square pyramidal Cu^{II} environments, the relevant exchange pathway through the im⁻ bridge is of the σ type. The imidazolato orbitals that are responsible for this kind of interaction are of the type sketched in Scheme 2; these are essentially parallel to the N–N' (or C=C) direction. Strict magnetostructural correlations have not been achieved for im⁻-bridged Cu^{II} systems.²⁶ However, among several structural parameters, two have mainly drawn attention:^{26,34,36} (i) the dihedral angles between the equatorial/basal Cu^{II} planes and the im⁻ ligand plane, and (ii) the Cu–N_{im} \cdots N_{im} angles. Theoretical studies³² have shown that magnetic exchange is more sensitive to the latter rather than to the former. It has been demonstrated^{32,37} that exchange



Scheme 2 Orientations of the orbitals relevant to the Cu^{II}–im–Cu^{II} magnetic exchange.

couplings are maximized when the Cu^{II}–N_{im} bonds are parallel to the imidazolato carbon–carbon bond, *i.e.* for Cu^{II}–N_{im} \cdots N_{im} angles close to 180° . Thus, the moderate coupling observed in **1** can be partly interpreted by the average Cu^{II}–N_{im} \cdots N_{im} angle value of 163.83° , which deviates significantly from 180° . However, since the experimental exchange coupling is a function of several structural and electronic factors,³⁵ any magnetostructural discussion cannot be reliable beyond this point.

Conclusions

The present work emphasises the ability of (im)₂CO to form new coordination polymers. The use of (im)₂CO in reactions with Cu^{II} and carboxylates in alcohols has provided access to two neutral, 1D polymeric species, one containing the bridging imidazolato(–1) ligand (**1**), and one containing the bridging terephthalate(–2) ligand and terminal imidazole groups (**4**·2*n*H₂O). It is noteworthy that we could not prepare these two compounds from conventional reactions employing Him as starting material. We have no reasons to believe that this research area is exhausted of new results. Indeed, ongoing studies are producing additional and interesting products, and our belief is that we have scratched only the surface of metal polymer chemistry based on (im)₂CO. As far as future perspectives are concerned, ‘analogues’ of **1** and **4** with other divalent 3d-metals are not known to date, and preliminary work shows that the preparation and stability of such polymers are dependent on the particular nature of the metal ion. In addition, the terminal monodentate ligands present in **1** (MeCO₂⁻, EtOH) and **4** (H₂O) could have future utility as sites for facile incorporation of neutral or anionic bis(monodentate) bridging ligands, *e.g.* azides, 4,4'-bipyridine *etc.*, as a means of accessing higher-dimensionality copper(II) polymers.

Acknowledgements

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