Copper(II) chloride/1-methylbenzotriazole chemistry: influence of various synthetic parameters on the product identity, structural and magnetic characterization, and quantum-chemical studies

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Abstract

A systematic investigation of the CuCl₂/Mebta (Mebta = 1-methylbenzotriazole) reaction system is described, involving the determination of the influence of the Cu II:Mehta ratio, the nature of solvent and the presence of counterions on the identity of the reaction products. As a consequence, complexes [Cu₂Cl₄(Mebta)₄] (1), [CuCl₂(Mebta)₂] (2), [Cu₂Cl₄(Mebta)₂]ₙ (3), [Cu₄OCl₆-(Mebta)₄] (4) and [Cu₂Cl₂(Mebta)₆](ClO₄)₂ (5) have been isolated and structurally characterized by single-crystal X-ray studies. Mebta behaves as a monodentate ligand binding through N(3). 1 is a dinuclear complex, the structure of 2 consists of discrete monomeric units, and that of 3 is composed of linear, well-separated polymeric chains of Cu II atoms. The molecules of 4 and 5 have a central μ₄-oxide ion surrounded tetrahedrally by four Cu II atoms. In the cations of 5 the two Cu II centres are asymmetrically bridged by two chloro ligands, with three Mebta molecules completing five coordination at each metal. Complexes were characterized by spectroscopic (IR, far-IR, solution UV/Vis) and thermal decomposition (TG, DTG, and DTA) techniques. Variable-temperature magnetic susceptibility data for 1, 3 and 5 showed intramolecular (1, 5) and intrachain (3) ferromagnetic exchange interactions. Estimates of the J parameters, experimentally derived, were in close agreement with a new magneto-structural criterion developed by us, holding for bis(l-chloro) copper(II) dimers. A comparison between the CuCl₂/Mebta and CuBr₂/Mebta systems is also presented.

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Keywords: Bis(l-chloro) copper(II) dimers; EHMO calculations; Ferromagnetic exchange interactions; (μ₄-oxo)hexakis(l-chloro)tetracopper(II) core; 1-Methylbenzo triazole copper(II) complexes; One-dimensional copper(II) coordination polymers

1. Introduction

Our longstanding interest in the syntheses and properties of 3d-metal complexes with benzotriazole (btaH, Fig. 1) and its derivatives as organic ligands [1–5] has been stimulated by a variety of factors, not least of
which is the relevance of this area to the protection of metal surfaces against wear and corrosion. The anticorrosion properties of btaH and its benzenesulfonyl-substituted derivatives toward certain metals, particularly copper and its alloys, are well established [6–8]. It has been postulated that copper oxide films are prerequisites for corrosion inhibition [9] and practical use of btaH as a corrosion inhibitor involves application to copper surfaces which have undergone some degree of oxidation. Despite the importance of benzotriazole corrosion inhibitors, no final conclusions have been reached of how they bind to oxidized metal surfaces, and why seemingly minor modifications in the structures of corrosion inhibitors can have a profound effect on their efficacy. Inorganic chemistry groups [10,11], including our group [1,4], have been investigating the mode of interaction of benzotriazoles with lightly oxidized metal surfaces by studying the coordination chemistry of these ligands with complexes of metal ions bound to oxygen-donor ligands. Garner’s and Tasker’s groups illustrated a new approach, based on the synthesis of polynuclear copper(II) benzotriazolato complexes containing β-diketonates as coligands, and the use of structural motifs found in such complexes to model relevant surface interactions, and hence understand the mode of action of benzotriazole inhibitors [10].

Another reason for the intense current interest in the coordination chemistry of benzotriazoles is the fact that benzotriazolate ligands are among the important players in the field of polynuclear transition metal chemistry. The development of routes and strategies for the synthesis of polynuclear complexes (clusters) of 3d metals (especially in moderate oxidation states) has been a subject of increasing interest over the last 15 years. These compounds provide a substantial impetus to several scientific areas, including bioinorganic chemistry, solid-state physics, molecular magnetism and material science [12–14]. For example, we have shown that the systematic investigation of the [Ni(β-diketonate)L2]-RbtaH or btaOH reaction mixtures has led to four families of polynuclear complexes: [Ni6(OH)2(acac)4(Rbta)4S4] [4], [Ni5(dbm)4(Rbta)2S4] [15], [Ni5(OH)2(acac)4(btaO)2S4] [1] and [Ni6(bzac)4(Rbta)2S4] [15] (acacH = acetylaceton; dbmH = dibenzoylmethane; L = H2O, EtOH; RbtaH = 5-methyl-, 6-methyl-, 5,6-dimethyl-, 5-chlorobenzotriazole or benzotriazole; S = solvate ligands). These complexes have novel structures and interesting magnetic properties. Recently, excellent synthetic work in Mn chemistry from Brechin’s group has resulted in the isolation of benzotriazolate-bridged Mn10[16], Mn10[16]Mn8[17] and Mn8[17] clusters with impressive structures and exciting magnetic properties, including [16] single-molecule magnet [13] behaviour.

1-Methylbenzotriazole (Mehta, Fig. 1) is not an efficient corrosion inhibitor. No coordination mode of Mebta other than monodentate binding through N(3) was found to occur in iron(III), cobalt(II), nickel(II), copper(II), palladium(II) and platinum(II) chemistries [3,5]. Thus, monodentate N(3) coordination can be regarded as the only coordination mode of Mebta and N(1)-substituted benzotriazoles (with groups containing no donor atoms). This monodentate coordination accounts in part for the lack of long-term corrosion inhibition on metals by Mebta [8]. For CuBr2 and Mebta, our studies showed [3] that the Mebta:CuII ratio and the nature of solvent affect the identity of the reaction products. Combined variations of these synthetic parameters led to the isolation of the complexes [{CuBr2(Mebta)}1 CuBr2(Mebta)2], [CuBr2(Mebta)-(MeCN)] and [CuBr2(Mebta)3]. We decided to study the CuCl2/Mebta reaction system to investigate the effect of halide substitution upon both the structural and physical properties of the resulting complexes. As far as the physical properties are concerned, differences might be expected. For instance, Hatfield, Hodgson and their coworkers, in their studies [18] on five-coordinate dinuclear bis(μ-chloro)copper(II) complexes of the types [CuCl2L2]- and [CuCl2(L–L)]2 (L and L–L are monodentate and bidentate chelating ligands, respectively), found a strong correlation between the exchange coupling constant, J, and the structural parameter ϕ/R (where ϕ is the Cu–Cl–Cu bridging angle and R is the longest bond in the Cu2(μ-Cl)2 unit). However, in the case of the bromo analogues, Landee and Greeney [19] showed that the dominant factor controlling superexchange strength is not related to the bridging angle but instead to the amount of distortion within the copper(II) basal plane; a later study by Romero et al. [20], however, showed that magnetic interaction strength can be correlated to the arrangement of the bridging bromo ligands around the metal.

In this report, we present our results from the full investigation of the CuCl2/Mebta reaction system. As we shall describe, we have found a number of synthetic parameters to have a great effect on the structure of obtained products. Detailed variable-temperature magnetic susceptibility and EPR studies will also be presented for three representative complexes, as well as a quantum-chemical interpretation of the exchange cou-
pling. Some preliminary results of this work have already been briefly communicated [21].

2. Experimental

2.1. Reagents and physical measurements

All manipulations were performed under aerobic conditions. Starting materials and solvents were commercially available and used without further purification. Mebta was purchased from Lancaster Synthesis Ltd.

Microanalyses (C, H, N) were performed by the University of Ioannina Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) data were obtained on Dupont R90 (equipped with a 951 TG analyser) and Seiko 200 TG/DTA instruments in a dinitrogen gas flow (50 cm³ min⁻¹); sample weights of 5–10 mg and heating rates of 1 and 5 °C min⁻¹ were used. IR spectra (4000–300 cm⁻¹) were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets. FT far-IR spectra were recorded on a Bruker IFS 113v spectrometer with samples prepared as polyethylene pellets. Solution electronic spectra (800–300 nm) were recorded on a Biochrom 4060 instrument. Variable-temperature (293–4.2 K) magnetic susceptibility measurements were carried out on polycrystalline samples by the Faraday method using a sensitive Sartorius M-25D electrobalance; the instrument was standardized with HgCo(NCS)₄. The applied magnetic field was 6.25 KOe. The experimental molar magnetic susceptibilities were corrected for the diamagnetic response using Pascal’s constants. The value of 60 × 10⁻⁶ cm³ mol⁻¹ was used for the TIP of the copper(II) ion. The magnetism of the samples was found to be field-independent. Variable-temperature (300–77 K) EPR spectra were recorded on a Bruker ER 200E-SRC X-band spectrometer; DPPH was used as an external standard. EPR spectra at the liquid He temperature were recorded on a Radiopan SE/X 2543 X-band spectrometer; DPPH was used as reference, and the magnetic field was calibrated with proton and lithium NMR probes.

Safety note. Benzotriazoles and their metal complexes are potentially explosive, and caution should be exercised in handling such compounds. However, the small quantities used in this study were not found to present a hazard.

2.2. Computational details

Calculations were carried out with the parametrization and methods already described [22]. In particular, EHMO SCC calculations [23–25] were performed on the [Cu₂Cl₄(NH₃)₄] model dimer in an attempt to determine the H₂S₈ of the atoms, by using the FORTICON MAC program [26]. The off-diagonal matrix elements were given by the expression of Wolfsberg–Helmholz [27]; still a value of 1.75 for the parameter K was used. The orbital exponents for the atoms were 1.625 for C, 1.95 for N, 2.033 for Cl, 1.30 for H, 2.05 and 1.325 for the 4s and 4p ones of Cu, respectively, as well as two-component 3d orbital of Cu with exponents of 5.95 and 2.30 and relative weights of 0.5933 and 0.5744, respectively.

2.3. Compound preparation

2.3.1. [Cu₂Cl₄(Mebta)₄] (1)

To a colourless solution of Mebta (0.25 g, 1.88 mmol) in EtOH (45 ml) was added a green solution of CuCl₂·2H₂O (0.16 g, 0.94 mmol) in the same solvent (45 ml). The green solution obtained was stirred at ambient temperature for 1–2 min and allowed to stand undisturbed for 24 h. Bluish green crystals of the product slowly appeared, which were collected by filtration, washed with EtOH (5 ml) and Et₂O (2 × 10 ml), and dried in air. Yield: 62%. Anal. Calc. for C₂₀H₂₆N₁₂Cl₄Cu₂: C, 42.0; H, 3.5; N, 21.0. Found: C, 41.8; H, 3.6; N, 20.4%. Crystals suitable for single-crystal X-ray crystallography were isolated by layering a solution of the product in MeOH with a mixture of Et₂O and n-hexane. Selected IR spectral data (KBr, cm⁻¹): 3053 w, 3037 m, 1497 m, 1480 s, 1392 m, 1269 s, 1140 m, 1052 s, 759 vs, 748 sh, 664 w. Selected far-IR spectral data (polyethylene, cm⁻¹): 299 sb, 271 sh, 265 m, 180 m, 162 s. UV/Vis spectral data (MeOH, kK): 26.52, 12.31. Complex 1 can also be prepared by employing Mebta:CuCl₂·2H₂O ratios of 8:1 and 4:1 in EtOH or MeOH.

2.3.2. [CuCl₂(Meba)₂] (2)

A slurry of CuCl₂·2H₂O (0.16 g, 0.94 mmol) in MeCN (50 ml) was refluxed for 5–6 h to give a clear yellow solution. This solution was added to a solution of Mebta (0.25 g, 1.88 mmol) in MeCN (20 ml) under stirring. The resulting green solution was left undisturbed at ambient temperature for 24 h and during this time bluish green crystals of 1 appeared. This material was completely transformed into X-ray quality green crystals of the product over a period of 3 days. The crystals were collected by filtration, washed with MeCN (2 × 10 ml) and Et₂O (210 ml), and dried in vacuo over silica gel. Yield: 63%. Anal. Calc. for C₁₄H₁₄N₆Cl₂Cu: C, 42.0; H, 3.5; N, 21.0. Found: C, 41.7; H, 3.3; N, 20.5%. Selected IR spectral data (KBr, cm⁻¹): 3057 w, 2932 w, 1494 w, 1458 m, 1385 s, 1222 s, 1132 m, 1050 s, 779 m, 750 s, 657 w. UV/Vis spectral data (MeOH, kK): 24.31, 11.50. Effective magnetic moment per copper(II): 2.12 BM at 22 °C. Complex 2 can also be isolated by employing Mebta:CuCl₂·2H₂O ratios of 8:1, 6:1, 4:1 and 1:1 in MeCN. The 8:1, 6:1, 4:1 and 1:1 reactions
in MeNO₂ also give complex 2 in completely similar procedures to those in MeCN (through the intermediate appearance of the bluish green crystals of 1). Employment of MeOH or EtOH as solvents can also lead to 2. The 8:1, 6:1, 4:1 and 2:1 reactions between Mebta and CuCl₂·H₂O in MeOH or EtOH give initially complex 1 under the conditions described above. When the reaction mixture is allowed to slowly concentrate at room temperature, green crystals of 2 also form. The not-too-dissimilar solubility of 1 and 2 prevents chemical separation. The two products are readily separated manually, washed with a little alcohol and Et₂O, dried in air and can individually be identified as complexes 1 and 2 by unit cell determination and spectral comparison with authentic materials.

2.3.3. [Cu₂Cl₄(Mebta)_2] ≃₃⁻ (3)

Method A. This compound was initially prepared as a powder by the thermal decomposition of the dinuclear complex [Cu₂Cl₄(Mebta)_4] (1). The TG/DTG/DTA curves of the latter showed a first endothermic weight loss between 150 and 203 °C, which corresponds to the elimination of two moles of Mebta per mole of 1 (Calc.: 33.2; Found: 32.1%). This first decomposition possibly consists of two overlapping steps as indicated (Calc.: 33.2; Found: 31.2%). This first decomposition loss between 150 and 203 °C gives a first endothermic weight loss with a shoulder in the main DTG peak. The 8:1, 6:1, 4:1 and 2:1 reactions between Mebta and CuCl₂·H₂O (0.20 g, 1.50 mmol) in the same solvent (20 ml). The resulting green solution was stirred for 5 min, and left capped and undisturbed for 2 weeks. This prolonged storage gave a mixture of bluish green prisms, brown prisms and brown needles. These different forms were carefully collected by filtration and dried in air. The three products were separated manually and individually identified as complexes 1 (by spectral comparison with authentic material), 3 (by unit cell determination) and 4 of the latter showed a first endothermic weight loss with a shoulder in the main DTG peak. These different forms were carefully collected by filtration and dried in air. The three products were separated manually and individually identified as complexes 1 (by spectral comparison with authentic material), 3 (by unit cell determination) and 4 of the latter showed a first endothermic weight loss with a shoulder in the main DTG peak.

Method B. CuO (0.09 g, 1.19 mmol) was added to a brown solution of CuCl₂ (0.32 g, 2.38 mmol) in MeOH (20 ml). The resulting brown slurry was refluxed for 24 h to give a cloudy brown “solution”. This was filtered and a solution of Mebta (0.40 g, 3.00 mmol) in MeOH (5 ml) added to the filtrate. No noticeable colour change occurred. The new solution obtained soon began to deposit a fine brown powder. The slurry was stirred until the reaction appeared complete and then filtered. The brown precipitate of the product was washed with cold MeOH (5 ml) and Et₂O (2 × 5 ml), and dried in air. Yield: 43%. Anal. Calc. for C₂₈H₂₄N₁₂O₁.2₅Cl₆Cu₄: C, 33.0; H, 2.8; N, 16.5. Found: C, 33.2; H, 2.9; N, 17.0%. Selected IR spectral data (KBr, cm⁻¹): 3058 w, 2942 w, 1497 m, 1460 m, 1392 m, 1303 s, 1141 m, 1120 w, 1057 m, 779 sh, 748 m, 664 w. Selected far-IR spectral data (polyethylene, cm⁻¹): 575 s, 274 m, 231 s, 191 w. UV/Vis spectral data (DMF, kK): 27.40, 22.95, 12.50.

2.3.4. [Cu₂OCl₆(Mebta)₄]·0.25H₂O (4 · 0.25H₂O)

Method A (in a mixture with complexes 1 and 3). A green solution of CuCl₂·H₂O (0.25 g, 1.47 mmol) in EtOH (40 ml) was added to a stirred solution of Mebta (0.20 g, 1.50 mmol) in the same solvent (20 ml). The resulting green solution was stirred for 5 min, and left capped and undisturbed for 2 weeks. This prolonged storage gave a mixture of bluish green prisms, brown prisms and brown needles. These different forms were carefully collected by filtration and dried in air. The three products were separated manually and individually identified as complexes 1 (by spectral comparison with authentic material), 3 (by unit cell determination) and 4 of the latter showed a first endothermic weight loss with a shoulder in the main DTG peak.

Method B. CuO (0.09 g, 1.19 mmol) was added to a brown solution of CuCl₂ (0.32 g, 2.38 mmol) in MeOH (20 ml). The resulting brown slurry was refluxed for 24 h to give a cloudy brown “solution”. This was filtered and a solution of Mebta (0.40 g, 3.00 mmol) in MeOH (5 ml) added to the filtrate. No noticeable colour change occurred. The new solution obtained soon began to deposit a fine brown powder. The slurry was stirred until the reaction appeared complete and then filtered. The brown precipitate of the product was washed with cold MeOH (5 ml) and Et₂O (2 × 5 ml), and dried in air. Yield: 43%. Anal. Calc. for C₂₈H₂₄N₁₂O₁.2₅Cl₆Cu₄: C, 33.0; H, 2.8; N, 16.5. Found: C, 33.2; H, 2.9; N, 17.0%. Selected IR spectral data (KBr, cm⁻¹): 3057 w, 2932 w, 1497 m, 1460 m, 1397 m, 1303 s, 1141 m, 1120 w, 1057 m, 779 sh, 748 m, 664 w. Selected far-IR spectral data (polyethylene, cm⁻¹): 575 s, 274 m, 231 s, 191 w. UV/Vis spectral data (DMF, kK): 27.40, 22.95, 12.50. Effective magnetic moment per copper(II): 1.90 BM at 20 °C.

2.3.5. [Cu₂Cl₂(Mebta)₆]/{ClO₄}₂⁻ (5)

To a stirred solution of Mebta (0.24 g, 1.80 mmol) in commercial concentrated hydrochloric acid (3 ml) was added a sky blue solution of CuCl₂·H₂O (0.12 g, 0.70 mmol) in H₂O (7 ml). The colour of the solution immediately changed to green. This was stirred, while an aqueous solution (2 ml) of NaClO₄·H₂O (0.15 g, 0.07 mmol) was added to give a new solution of the same colour. The reaction flask was allowed to stand undisturbed at ambient temperature for 10–12 h. During this time X-ray quality green crystals of the product formed. The crystals were collected by fil-
tration, washed with EtOH (3 × 10 ml) and dried in vacuo over silica gel. Yield: 57%. Anal. Calc. for C_{42}H_{42}N_{18}O_{6}Cu_{2}: C, 42.2; H, 3.5; N, 21.1. Found: C, 42.1; H, 3.4; N, 20.7%. Selected IR spectral data (KBr, cm⁻¹): 3052 w, 2935 w, 1502 m, 1460 s, 1397 m, 1230 s, 1146 s, ~1100 sb, 785 s, 748 s, 664 w, 630 s. Selected far-IR spectral data (polyethylene, cm⁻¹): 275 sb, 188 m, 167 s. UV/Vis spectral data (DMF, kK): 27.02, 23.00, 12.20.

2.4. X-ray crystallography

Data collection, crystal data and structure solution information are listed in Table 1. Diffraction measurements for compounds 1, 3, 4 · 0.25H₂O, and 5 were performed on a P2₁, Nicolet diffractometer using Zr-filtered Mo Kα radiation, while for compound 2 the data collection was performed on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo Kα radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred reflections. Intensity data were recorded using a 0–2θ scan. Three standard reflections monitoring every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization and Ψ-scan absorption corrections (for 1–4 only) were applied.

The structures were solved by direct methods using SHELXS-86 [28] and refined by full-matrix least-squares techniques of F² with SHELXL-97 [29]. For 1, 2, 3 and 5 all H atoms were located by difference maps and refined isotropically; all non-H atoms were refined with anisotropic thermal parameters. For 4 · 0.25H₂O all H atoms were located by difference maps and refined isotropically, except those on the methyl groups which were introduced at calculated positions as riding on bonded atoms; all non-H atoms were refined anisotropically, except the oxygen of the solvate H₂O molecule which was refined isotropically.

3. Results and discussion

3.1. Syntheses

The product identity of the CuCl₂ · 2H₂O/Mehta reaction systems depends mainly on the metal:ligand reaction ratio and the nature of the solvents. The various synthetic procedures and transformations described in detail in Section 2.3 are conveniently summarized in the stoichiometric chemical Eqs. (1)–(8). It should be pointed out that Eqs. (2) and (4) represent chemical equilibria in solution, while Eq. (3) [which, at first
Selected interatomic distances and angles for complexes 4 and 6 are listed in Tables 2–4, 6 and 8, respectively. Labelled ORTEP plots of these complexes are shown in Figs. 2–6. There are two common features in the five structures. Firstly, Mebta behaves as a monodentate ligand with the nitrogen atom of position 3 (Fig. 1) being the ligated atom; secondly, the molecules of Mebta are essentially planar, the deviations of atoms from the least-squares plane through them being less than 0.02 Å.

The crystal structure of 1 consists of isolated dinuclear molecules with two bridging chloro ligands; a terminal chloride and two nitrogen atoms from two trans-Mebta ligands complete five-coordination at each metal ion. The bridging CuCl(1)CuCl(1′) unit is strictly planar, with a crystallographically imposed inversion centre.

<table>
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<th>Table 2</th>
<th>Selected interatomic distances (Å) and angles (°) for complex 1</th>
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<tr>
<td>Cu–Cl(1)</td>
<td>2.302(1) Cu–N(3) 2.021(1) Cu–Cl(1′) 2.629(1) Cu–N(3′) 2.023(1)</td>
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<tr>
<td>Cu–Cl(2)</td>
<td>2.273(1) Cu–Cl(1′) 3.437(1) Cu–Cl(2) 2.523(1) Cu–Cl(2′) 3.429(1)</td>
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<tr>
<td>Cl(1)–Cu–Cl(1′)</td>
<td>91.9(1) Cl(1)–Cu–N(3) 89.1(1) Cl(1)–Cu–N(3′) 89.1(1)</td>
</tr>
<tr>
<td>Cl(1)–Cu–N(3)</td>
<td>94.3(1) Cl(1)–Cu–N(3′) 94.3(1) Cl(1)–Cu–N(13) 172.3(1)</td>
</tr>
<tr>
<td>Cl(1)–Cu–Cl(1′)</td>
<td>100.5(1) Cl(1)–Cu–N(13) 90.1(1) Cl(1)–Cu–Cl(2) 91.9(1)</td>
</tr>
<tr>
<td>Cl(1)–Cu–N(3′)</td>
<td>94.3(1) Cl(1)–Cu–Cl(2) 91.9(1) Cl(1)–Cu–N(3) 89.0(1)</td>
</tr>
<tr>
<td>Symmetry code: ′ = −x, −y, −z + 1.</td>
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<td>Cu–Cl(1)</td>
<td>2.228(2) Cu–N(3) 1.981(2)</td>
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<td>Cu–Cl(2)</td>
<td>2.230(2) Cu–N(13) 1.990(2)</td>
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<tr>
<td>Cl(1)–Cu–Cl(2)</td>
<td>143.7(1) Cl(2)–Cu–N(3) 94.8(1)</td>
</tr>
<tr>
<td>Cl(1)–Cu–N(3)</td>
<td>93.8(1) Cl(2)–Cu–N(13) 93.6(1)</td>
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<tr>
<td>Cl(1)–Cu–N(13)</td>
<td>95.0(1) N(3)–Cu–N(13) 152.3(1)</td>
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<tr>
<th>Table 4</th>
<th>Selected interatomic distances (Å) and angles (°) for complex 3</th>
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<tr>
<td>Cu(1)–Cl</td>
<td>2.661(1) Cu(2)–N(3) 1.986(2)</td>
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<tr>
<td>Cu(2)–Cl</td>
<td>2.534(1) Cu(1)–Cu(2) 3.556(1)</td>
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<td>Cl(1)–Cu(1)–Cl(2)</td>
<td>90.3(1) Cl(1)–Cu(2)–N(3) 89.4(1)</td>
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<tr>
<td>Cl(1)–Cu(1)–N(3)</td>
<td>78.5(1) Cl(1)–Cu(1)–Cl(2) 95.6(1)</td>
</tr>
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Fig. 2. Partially labelled ORTEP representation of the dinuclear molecule of complex 1 at the 30% probability level. Primed and unprimed atoms are related by the crystallographic inversion centre.
centre in the middle of the dimer. The geometry at each CuII centre is square pyramidal (sp) with the basal plane comprising the two trans-nitrogen atoms and two trans-chloride ions [Cl(1) and Cl(2) for Cu]; the apical position is occupied by the chloro ligand [Cl(1') for Cu] which is basal to the other copper (Cu') in the dimer.

The in-plane Cu–Cl distances of 2.273(1) and 2.302(1) Å are within the normal range, with the distance to the bridging chlorine slightly longer, as expected. The Cu...Cu' separation [3.437(1) Å], the out-of-plane Cu–Cl(1') distance [2.629(1) Å] and the bridging Cu–Cl(1)–Cu' angle [88.1°] in 1 are all towards the low end of the respective ranges observed for other, structurally similar square-pyramidal dichloro-bridged copper(II) dimers [18,30–33].

The Mebta ligands in syn positions are nearly parallel, the angle between their mean planes being 4.3°. There appear to be intradimer stacking interactions between these ligands on the two sides of the molecule; the shortest distance from the mean plane of N(1), N(2), and N(3)–containing Mebta ligands is 3.50 Å for N(12').

Complex 1 joins a rather large family of structurally characterized complexes of the type [Cu2Cl2(μ-Cl)Lx] (x = 2, 4) [18,30–33]. However, most members of this family contain bidentate chelating ligands Ls (x = 2); complexes containing monodentate aromatic N-donors

Fig. 3. Molecular structure of 2 with the atom labelling scheme. The atoms are drawn at the 30% probability level.

Fig. 4. A small portion of the chain present in complex 3. Carbon atoms are not labelled; identical labels are used for symmetry-generated atoms. The atoms are drawn at the 30% probability level.
(\(x = 4\)) are rare, a typical example being [Cu\(_2\)Cl\(_4\)(2-pic)\(_4\)] (2-pic = 2-methylpyridine) [32]. In this complex, the apical Cu–Cl bond [3.364(1) \(\text{Å}\)] is extremely long and longer than that found in any other square-pyramidal dichloro-bridged copper(II) dimer.

The Cu\(^{II}\) atom in the mononuclear complex 2 is surrounded by two nitrogen atoms and two terminal chloro ligands. The geometry about the copper ion is best described as tetrahedrally distorted \(\text{trans}\)-square planar. The \(\text{cis}\) [93.6(1)–95.0(1)\(^{\circ}\)] and \(\text{trans}\)-angles [143.7(1) and 152.3(1)\(^{\circ}\)] of all ligands around the metal ion are intermediate between the expected values for tetrahedral (109.47\(^{\circ}\)) and square planar (90\(^{\circ}\), 180\(^{\circ}\)), respectively. The two Cu–Cl distances [2.228(2) and 2.230(1) \(\text{Å}\)] are typical for terminal Cu–Cl bonds [34]. The Cu–N distances [1.981(2) and 1.990(2) \(\text{Å}\)] are very close to the
Cu–N bond lengths of 1.968(4) and 1.970(4) Å in the isostructural complex [CuBr₂(Mehta)]$_2$ [3].

A very close precedent to 2 is complex [CuCl₂(mim)$_2$] (mim = N-methylimidazole), in which the average Cu–Cl and Cu–N bond lengths, and the Cl–Cu–Cl and N–Cu–N angles are 2.258(3), 1.969(5) Å, 143.6(1) and 149.7(1)$^\circ$, respectively [34].

The crystal structure of complex 3 is composed of well-separated, linear chains of Cu$^{II}$ atoms bridged asymmetrically by two chloro ligands. A regular alternation of two non-equivalent copper(II) ions (Cu(1) and Cu(2)) occurs in the chain: Cu(1) is surrounded by four chlorides in an almost perfect square-planar environment, whereas Cu(2) exhibits a compressed, trans-octahedral (μ-Cl)$_4$N$_2$ environment. There is a mirror plane through Cu(2) and the Mehta ligands, and a second one, parallel to the first, through Cu(1), as well as a twofold crystallographic axis perpendicular to the mirror planes through Cu(1) and Cu(2). Thus, each Cu$^{II}$ atom is located on a crystallographic centre of symmetry; the two local inversion centres result in only one crystallographically independent chloride atom and Mehta ligand. The Cu(1)–Cl bond distance [2.261(1) Å] is noticeably shorter than the Cu(2)–Cl bond length [2.534(1) Å], consistent with the lower coordination number for Cu(1).

The doubly bridged chain with two alternating chromophores observed in 3 is unique for complexes of the formulation CuX$_2$L (X = Cl or Br, L = monodentate ligand). Most of the bis(μ-Cl) 1D copper(II) complexes have the formulations CuCl$_2$L$_2$ or CuCl$_2$(L–L), where L–L is a bidentate chelating ligand, and contain exclusively six-coordinate metal ions. In Table 5 are compared selected structural parameters for 3 and representative bis(μ-chloro) copper(II) chains of the general formula [(CuCl$_2$L)$_2$]$_n$. Complex 3 exhibits the shortest Cu–Cl and Cu...Cu distances and the largest Cu–Cl–Cu angle.

It should be pointed out at this point that powders of empirical formulae CuCl$_2$(Mehta)$_2$ and CuCl$_2$(Mebta) have been known since 1983 when Reedijk et al. [11] isolated them from the reactions of CuCl$_2$·2H$_2$O and Mehta in EtOH/n-pentane. The authors proposed a chloro-bridged linear-chain structure with two monodentate Mehta ligands per Cu$^{II}$ for the 1:2 complex, and suggested a bidentate bridging mode of Mehta in the 1:1 compound; with hindsight, it seems that the 1:1 compound is complex [(CuCl$_2$(Mehta)$_2$)]$_n$ (3).

The crystal structure of 4 · 0.25H$_2$O is composed of [CuClO$_4$(Mehta)$_2$] molecules and water solvate molecules; the latter will not be further discussed. The molecule [CuClO$_4$(Mehta)$_2$] consists of a tetrahedron of Cu$^{II}$ atoms held together by one central μ₄-oxide ion and six μ-chloro ligands; each chloride spans an edge of the tetrahedron. One Mehta molecule is bound to each Cu$^{II}$ atom in a terminal fashion. The μ₄-oxo group and two of the bridging chloro ligands [Cl(3), Cl(4)] lie on a twofold axis. The Cu(μ₄-O) tetrahedron is almost regular, the Cu...Cu distances being between 3.103(4) and 3.152(3) Å, and the Cu–O–Cu angles varying from 108.6(1) to 110.9(2)$^\circ$. The central μ₄-O$^{2-}$ ligand is linked asymmetrically to Cu$^{II}$ ions, the individual bond lengths being 1.908(3) and 1.914(3) Å. The chloro bridges involving Cl(1) and Cl(2) [and their symmetry partners] are slightly asymmetrical, with Cu–Cl distances ranging from 2.378(2) to 2.449(2) Å; the greatest asymmetry occurs for the Cu(1)–Cl(2)–Cu(2’) system. Angles at the bridging chloride ions are all acute, with individual values ranging from 80.0(1)$^\circ$ to 82.5(1)$^\circ$.

The six chloro ligands comprise a rather distorted octahedron around the central oxide ion; the Cl...Cl, O...Cl distances and cis Cl...O...Cl angles vary as follows: O...Cl = 2.882(2)–2.953(2) Å, Cl...Cl = 3.982(3)–4.248(3) Å, Cl...O...Cl = 86.5(2)–93.5(2)$^\circ$. These variations, however, are not as large as those observed in the structurally similar complexes [Cu$_6$Cl$_{12}$-ppy)$_4$] (O...Cl = 2.92–2.96 Å, Cl...Cl = 3.93–4.41 Å, Cl...O...Cl = 84–98$^\circ$) [39] and [Cu$_4$Cl$_6$(2-pic)$_4$] (O...Cl = 2.87–3.03 Å, Cl...Cl = 3.73–4.55 Å) [40], where inter- and intramolecular steric hindrances were postulated as reasons for the distortions in the chloride octahedron (py = pyridine, 2-pic = 2-methylpyridine).

Each of the Cu$^{II}$ atoms is in a slightly distorted trigonal bipyramidal coordination environment, with the chloro ligands in the three equatorial sites. The Cu$^{II}$ atoms are displaced out of the planes of their respective equatorial chlorides by 0.212(3) [Cu(1), Cu(1’)] and 0.212(3) [Cu(2), Cu(2’)] Å in the directions of the donor nitrogen atoms. The N–Cu–Cl angles range from 91.4(2) to 101.0(2)$^\circ$, whereas the O–Cu–Cl angles are significantly smaller [83.5(1)–86.4(1)$^\circ$. The equatorial

Table 5

Comparison of selected structural parameters (Å, $^\circ$) for [(CuCl$_2$(Mehta)$_2$)]$_n$ (3) and representative bis(μ-chloro) 1D copper(II) complexes of the general formula [(CuCl$_2$L)$_2$]$_n$ (L = monodentate ligand)

<table>
<thead>
<tr>
<th>Compound*</th>
<th>Cu–Cl</th>
<th>Cu...Cu</th>
<th>Cu–Cl–Cu</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CuCl$_2$(py)$_2$)]$_n$</td>
<td>3.026, 2.299</td>
<td>3.870</td>
<td>88.5</td>
<td>[35]</td>
</tr>
<tr>
<td>[(CuCl$_2$(4-V-py)]$_n$</td>
<td>3.100, 2.310</td>
<td>3.910</td>
<td>91.5</td>
<td>[36,37]</td>
</tr>
<tr>
<td>[(CuCl$_2$(4-Et-py)]$_n$</td>
<td>3.210, 2.280</td>
<td>4.000</td>
<td>91.9</td>
<td>[37]</td>
</tr>
<tr>
<td>[(CuCl$_2$(2)-py)]$_n$</td>
<td>2.998, 2.322</td>
<td>3.853</td>
<td>91.9</td>
<td>[38]</td>
</tr>
<tr>
<td>[(CuCl$_2$(Mehta)]$_n$</td>
<td>2.534, 2.261</td>
<td>3.556</td>
<td>95.6</td>
<td>this work</td>
</tr>
</tbody>
</table>

* Abbreviations: py, pyridine; 4-V-py, 4-vinylpyridine; 4-Et-py, 4-ethylpyridine; tz, triazole.
Cl–Cu–Cl angles vary from 112.0(1)° to 127.0(1)°, and the N–Cu–O angles are 177.4(2)° and 175.5(2)° for Cu(1) and Cu(2), respectively.

Several structurally characterized examples of complexes containing the [Cu^II](μ₄-O)(μ-X)₆ core (X = Cl, Br) are now available. Since Bertrand and Kelley [41] and tom Dieck and co-workers [42] characterized the first tetranuclear copper(II) complexes of the general formula [Cu₄OX₁₀−₆L₄]⁻⁴, where L represents a monodentate ligand, a number of these compounds with the specific formula [Cu₄OX₁₀−₆L₄] have been synthesized. All these complexes have the same structural motif, with four Cu^II^ atoms at the corners of a tetrahedron around the central μ₄-O²⁻ group and six doubly bridging halogeno ions over each edge of the tetrahedron. In Table 7 are compared selected structural parameters for 4 · 0.25H₂O and the representative complex [Cu₄OCl₆(Hdmppz)₄], where Hdmppz is 3,4-dimethyl-5-phenylpyrazole [43]; the comparison reveals that the structural similarity between these complexes is impressive.

Table 6
Selected interatomic distances (Å) and angles (°) for complex 4 · 0.25H₂O

<table>
<thead>
<tr>
<th>Distance/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)–Cl(1)</td>
<td>2.434(2)</td>
</tr>
<tr>
<td>Cu(1)–Cl(2)</td>
<td>2.378(2)</td>
</tr>
<tr>
<td>Cu(1)–Cl(4)</td>
<td>2.370(2)</td>
</tr>
<tr>
<td>Cu(1)–N(3)</td>
<td>1.970(5)</td>
</tr>
<tr>
<td>Cu(1)–O</td>
<td>1.898(3)</td>
</tr>
<tr>
<td>Cl(1)–Cu(2)</td>
<td>2.372(2)</td>
</tr>
<tr>
<td>Cl(1)–Cl(2)</td>
<td>2.390(2)</td>
</tr>
<tr>
<td>Cl(1)–Cl(3)</td>
<td>1.985(5)</td>
</tr>
<tr>
<td>Cl(2)–Cu(2)</td>
<td>2.514(2)</td>
</tr>
<tr>
<td>Cl(2)–O</td>
<td>1.921(5)</td>
</tr>
<tr>
<td>O–Cu(3)</td>
<td>1.943(4)</td>
</tr>
<tr>
<td>Cl(3)–Cu(3)</td>
<td>1.817(4)</td>
</tr>
<tr>
<td>O–Cu(4)</td>
<td>1.882(2)</td>
</tr>
<tr>
<td>Cl(4)–Cu(4)</td>
<td>1.953(2)</td>
</tr>
</tbody>
</table>

Symmetry code: ′ = −x + 1/2, −y + 1/2, z.

Table 7
Comparison of selected structural parameters (Å, °) for complex [Cu₄OCl₆(Mepta)₄] · 0.25H₂O (4 · 0.25H₂O) and complex [Cu₄OCl₆(Hdmppz)₄]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>4 · 0.25H₂O</th>
<th>[Cu₄OCl₆(Hdmppz)₄]²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Cu</td>
<td>3.103–3.152</td>
<td>3.079–3.173</td>
</tr>
<tr>
<td>Cu–O</td>
<td>1.908, 1.913</td>
<td>1.905, 1.913</td>
</tr>
<tr>
<td>Cu–N</td>
<td>1.970, 1.985</td>
<td>1.960, 1.964</td>
</tr>
<tr>
<td>Cu–Cl</td>
<td>2.370–2.449</td>
<td>2.352–2.499</td>
</tr>
<tr>
<td>Cu–O</td>
<td>108.6–110.9</td>
<td>107.4–112.4</td>
</tr>
<tr>
<td>Cu–Cl</td>
<td>80.0–82.5</td>
<td>78.8–81.9</td>
</tr>
<tr>
<td>Cu–Cl</td>
<td>112.0–127.0</td>
<td>118.0–121.3</td>
</tr>
<tr>
<td>N–Cu–O</td>
<td>175.5, 177.4</td>
<td>175.8, 176.3</td>
</tr>
</tbody>
</table>

Complex 5 crystallizes in the triclinic space group P̅1. Its crystal structure consists of dinuclear [Cu₂Cl₂(Mepta)₄]²⁻ cations and ClO₄⁻ counterions; the latter will not be further discussed. The two Cu^II^ centres are asymmetrically bridged by two chloro ligands; three monodentate Mepta molecules complete five-coordination at each metal. The bridging Cu₂Cl₂ unit is constrained to be planar by the presence of a crystallographic inversion centre in the middle of the dimer. The Cu–Cl bond lengths in this compound [2.327(1) and 2.554(1) Å] are comparable to the two bridging Cu–Cl bond lengths found in 1 [2.302(1) and 2.629(1) Å]. The Cu–N distances [2.001(2)–2.026(2) Å] are nearly identical to the values of 2.021(1) and 2.023(1) Å observed in 1.

The five donor atoms within bonding distances do not define a regular polyhedron around copper. Analysis of the shape-determining angles using the approach of Reedijk and co-workers [44] yields a value for trigonality index, τ, of 0.5 (τ = 0 and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively). Thus, the geometry about Cu(1) [Cu(1)'] is significantly distorted and can be described as either distorted tp or distorted sp. With use of the tp description the axial sites of Cu(1) are occupied by N(23) and Cl(1'), with atoms N(3), N(13) and Cl(1) making up the equatorial plane. The equatorial bond angles are 103.1(1)°, 109.8(1)° and 147.0(1)°. The rather large steric hindrance caused by the size of the two “equatorial” Mepta can be one reason for the large N(3)–Cu(1)–N(13) angle of 147.0(1)°. For the sp description the basal plane would consist of the atoms N(3), N(13), N(23) and Cl(1'), with Cl(1) occupying the apical site.

The closest precedent to 5 is complex [Cu₂−(μ-Cl)₂(dien)₂][ClO₄]₂ [45], where dien is diethylenetriamine; in the latter each Cu^II^ atom is surrounded by...
Diagnostic IR, far-IR and solution electronic spectroscopy, and thermal decomposition data

Diagnostic IR, far-IR and solution electronic spectral data of complexes 1–5 are given in Table 9. The IR spectrum of free Mebta exhibits two bands at 1197 and 1110 cm⁻¹ associated with the ν(N=N) and ν(N–N) modes of vibration, respectively [3,5]. These bands are shifted to 1220–1230 and ~1140 cm⁻¹, respectively, in the spectra of the complexes. These shifts are compatible with N(3) being the donor atom to copper(II) [3,5]. The coordinated Mebta is considered responsible for the two bands at ~780 and 750 cm⁻¹ in 2–5; the latter is stronger and assigned as a C–H out-of-plane vibration and the former is due to a vibration involving both benzene and triazole in-plane bending [10]. These modes coincide at 759 cm⁻¹ in the spectrum of 1. The spectrum of 5 exhibits strong bands at 1100 and 630 cm⁻¹ due to the ν_{d–d}(F₂)[ν_{d–d}(Cl–O)] and ν_{d–d}(F₂)[δ_{d–d}(OClO)] of the uncoordinated ClO₄⁻ [46].

Assignments of metal–ligand stretching vibrations in Table 9 have already been described in part 2.3.3. The intermediate formed (proved to be complex 3) decomposes in two successive, endothermic steps between 215 and 295 °C.

Table 9

<table>
<thead>
<tr>
<th>Assignment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4 · 0.25H₂O</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR/far-IR (cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν(N=N)</td>
<td>1230 s</td>
<td>1222 s</td>
<td>1225 s</td>
<td>1230 s</td>
<td>1230 s</td>
</tr>
<tr>
<td>ν(N–N)</td>
<td>1140 m</td>
<td>1132 m</td>
<td>1141 m</td>
<td>1141 w, 1125 w</td>
<td>1146 s</td>
</tr>
<tr>
<td>ν₂(ClO₄⁻)</td>
<td></td>
<td></td>
<td></td>
<td>~1100 s</td>
<td>630 s</td>
</tr>
<tr>
<td>ν₄(ClO₄⁻)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν(Cu–O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>575 s</td>
</tr>
<tr>
<td>ν(Cu–Cl)ᵦ</td>
<td>299 sb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν(CuCl)ᵦ</td>
<td>180 m, 162 s</td>
<td></td>
<td></td>
<td>175 sh, 159 s</td>
<td>231 s, 191 w</td>
</tr>
<tr>
<td>ν(Cu–N)</td>
<td>271 sh, 265 m</td>
<td></td>
<td>287 s</td>
<td>274 m</td>
<td>275 sb</td>
</tr>
<tr>
<td>UV/VIS (kK)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMCT</td>
<td>26.52d</td>
<td>24.31d</td>
<td>30.95°, 22.95°</td>
<td>27.40 shf</td>
<td>27.02e</td>
</tr>
<tr>
<td>d–d</td>
<td>12.31d</td>
<td>11.50f</td>
<td>~12.50f</td>
<td>12.60f</td>
<td>12.20e</td>
</tr>
</tbody>
</table>

Abbreviations: b, broad; LMCT, ligand-to-metal charge transfer; m, medium; ν(CuCl)ᵦ, stretching frequency of the bridging Cl–Cl bond; ν(Cu–Cl), stretching frequency of the terminal Cu–Cl bond; b, broad; m, medium; s, strong; sh, shoulder; w, weak.

No far-IR data are available for this complex.
Possibly overlapping with a vibration of Mebta.
In MeOH.
In DMF.
In MeCN.
according to Eq. (9). Weight loss calculations indicate that the final residue at 600 °C is CuO. Complex 3 is thermally stable up to 215 °C; its decomposition pattern above 215 °C is almost identical with that of the intermediate obtained from the decomposition of 1 at 205–215 °C, as expected.

\[
\{[\text{Cu}_2\text{Cl}_6(\text{Mehta})_2]\}_n \\
\xrightarrow{215-293^\circ C} 2n\text{CuCl}_2 + 2n\text{Mehta} \uparrow
\] (9)

Complex 4 · 0.25H$_2$O decomposes endothermically between room temperature and 440 °C according to the tentative scheme described by Eq. (10). The pattern above this temperature is rather simple involving slight increase of weight (possibly due to slow oxidation). A strong endothermic DTA peak at 550 °C, not accompanied by a weight change, may be due to partial melting or to a phase transition. The unstable reaction above this temperature is rather simple involving the formation of no stoichiometric compounds could be assigned to the TG curve with overlap-ting degradation processes. The absence of TG plateau indicates that stable intermediates cannot be formed. No stoichiometric compounds could be assigned to the TG curve’s inflections. The final residue at 600 °C appears to be CuO.

3.4. Magnetic and EPR studies of complexes 1, 3 and 5

Variable-temperature magnetic susceptibility ($\chi_M$) data were collected for powdered samples of 1, 3 and 5 in the temperature range 4.2–296 K.

Data for 1 are shown in Fig. 7. The product $\chi_M T$ increases upon cooling, from 0.417 cm$^3$K mol$^{-1}$ at 294 K to 0.454 cm$^3$K mol$^{-1}$ at 4.2 K, which, together with the positive Weiss temperature ($\theta = +0.3$ K and $\theta = +3.1$ K in the 4.2–294 K and 50–294 K temperature ranges, respectively), is consistent with intramolecular ferromagnetic coupling. Hence, the experimental data between 4.2 and 294 K have been fitted to the Bleaney–Bowers equation [47] with a molecular-field correction [48], namely:

\[
\chi_M = \frac{1}{N} \frac{1}{kT} [1 + 1/3e^{-2J/kT}]^{-1},
\] (12)

($g$) is the average splitting factor obtained from the fitting procedure, $z$ is the number of the nearest neighbouring dimers in the crystal lattice, $J$’ is the interdimer exchange parameter, while the other symbols have their usual meaning. The best fitting parameters obtained are $2J = +6.7$ cm$^{-1}$ and $zJ' = -1.2$ cm$^{-1}$ and $g = 2.137$ by minimizing the function $R$ [Eq. (13)] to 4.46 × 10$^{-3}$.

\[
R = \sum_{i=1}^{n} \left[ (\chi_M)_i^{\exp} - (\chi_M)_i^{\calc} \right] / (\chi_M)_i^{\exp} \sum_{i=1}^{n} 1/[(\chi_M)_i^{\exp}]^2
\] (13)

The X-band EPR spectrum of a powdered sample of 1 is axial ($g_\parallel = 2.210$, $g_\perp = 2.078$, $g = 2.123$) and remains unchanged in the 77–300 K temperature range.

Complex 5 exhibits a very similar magnetic and EPR behaviour with that of 1 (Fig. 8). Upon cooling, the product $\chi_M T$ increases, reaches a maximum of 0.546 cm$^3$ K mol$^{-1}$ at 4.2 K which, along with the positive Curie–Weiss temperature ($\theta = +0.9$ K in the 4.2–296 K and $\theta = +4.2$ K in the 50–296 K range), is indicative of intramolecular ferromagnetic interaction. Consequently, we used the same exchange Hamiltonian and the susceptibility expressions provided by Eqs. (11) and (12) as for 1. The experimental magnetic susceptibility data in the 4.2–296 K range were least-squares fitted to Eq. (11) to give the parameters $2J = +10.4$ cm$^{-1}$, $zJ' = -0.5$ cm$^{-1}$ and $g = 2.187$ by minimizing the factor $R$ [Eq. (13)] to 5.52 × 10$^{-3}$.
The X-band EPR spectrum of a powdered sample of 1 is also axial ($g_{\parallel} = 2.321$, $g_{\perp} = 2.043$, $g = 2.140$) and remains unchanged in the 77–300 K temperature range.

For complex 3, the product $\chi_M T$ (Fig. 9) increases upon cooling, reaches a maximum of 0.621 cm$^3$ K mol$^{-1}$ at ca. 20 K and then decreases to 0.563 cm$^3$ K mol$^{-1}$ at 4.3 K. The compound follows the Curie–Weiss law, $\chi_C = 0.471/(T - 12.4)$, in the higher temperature range ($T > 50$ K). Taking into account the crystal structure of the complex (see above), the magnetic data were fitted to the Heisenberg model of the magnetic interaction (Padé expansion series [49–51] for $S = 1/2$) assuming a first-order molecular-field correction to account for the interchain interactions. The analytical expression for the susceptibility is given by Eq. (14):

$$\chi_{\text{corr}} = \frac{\chi_C}{1 - 2zJ'/g_z}.$$  

(14)

The term $\chi_C$ is the susceptibility of a Heisenberg chain given by Eq. (15):

$$\chi_C = \frac{N\beta^2 g^2 L}{4kT} \left( \frac{1}{M} \right)^{2/3},$$

where,

$$L = 1 + 5.7979916K + 16.902653K^2 + 29.376855K^3 + 29.832959K^4 + 14.036918K^5,$$

and

$$M = 1 + 2.7979916K + 7.0086780K^2 + 8.6538644K^3 + 4.5743114K^4, \quad K = J/2kT,$$

$z$ is the number of the nearest neighbouring chains, $J'$ is the interchain exchange parameter, and $g$ is the spectroscopic splitting parameter. The best fitting parameters obtained are $J = 7.8$ cm$^{-1}$ and $zJ' = -3.5$ cm$^{-1}$ and $g = 2.290$ with an $R$ value [Eq. (13)] of $1.38 \times 10^{-4}$. Consequently, complex 3 constitutes an interesting example of a molecular ferromagnet in which chains are coupled antiferromagnetically.

The X-band EPR spectrum of a powdered sample of 3 is isotropic in the whole temperature range (4.2–293 K). The peak to peak linewidth of the signal increases upon cooling ($\delta H_{pp} = 290, 355$ and $477$ G at 293, 77 and 4.2 K, respectively). Spectroscopic splitting parameter value taken from the EPR spectra of the complex is 2.15.

3.5. Quantum-chemical interpretation of the exchange coupling for complexes 1 and 5

First of all it is important to emphasize that the positive values of $2J$ for complexes 1 and 5 are the highest yet reported for a member of this class of bis(μ-chloro) copper(II) dimers (Table 10).

It was shown in Section 3.2 that the Cu$^{II}$ atoms in 1 are in regular square-pyramidal surroundings, whereas the coordination polyhedron in 5 can be characterized as intermediate between a trigonal bipyramid and a square pyramid ($\tau = 0.5$ [44]). Consequently, 1 belongs to the square-pyramidal apical-basal type I (Scheme 1), while 5 may be considered as a trigonal bipyramidal axial-equatorial dimer of type II (Scheme 1). It is well-known that in the type-I and -II geometries, the unpaired electron lies predominantly in a $|x^2 - y^2\rangle$- or a $|z^2\rangle$-type orbital, respectively. Hatfield and coworkers have shown [18] that this distinction is unnecessary for the two types, since they are interconvertible by a single angular deformation (of a kind of the Berry mechanism for intramolecular rearrangement). Thus, electronically the observed dimers of types I and II are substantially similar and, in fact, the tbp (type II) complexes exhibit a predominantly $|x^2 - y^2\rangle$ ground state [18,60] as expected for sp geometry; consequently, all complexes in Table 10 may be viewed as belonging to the same structural type and their magnetic properties can be compared directly [18].

As already stated in Section 1, a strong correlation has been found [18] between the singlet–triplet splitting
Calculations were performed on the general model trimethylethylenediamine.

$^{13} \text{[Cu}_2\text{Cl}_8\text{]}^4-$ridine; Pypep, the monoanion of $^{12} \text{[Cu}_2\text{Cl}_2\text{(Mebta)}_6\text{]}^{2+}$ (Scheme 2) and $^{10} \text{[Cu}_2\text{Cl}_4\text{(L–L)}_2\text{]}$ complexes ($^{33}$). This value is in profound contrast to the experimental one ($^{2} \text{[Cu}_2\text{Cl}_4\text{(tmen)}_2\text{]}$). In an attempt to investigate this discrepancy, the Cl–Cl interactions are the three major structural factors governing the exchange interaction are the $\phi$ and $\omega$ angles, and the $R$ bond distance. For the study of the $\phi$, $R$ dependence of the $e_A - e_O = \delta$ difference, where $\delta$ denotes the energy difference between the symmetric and antisymmetric MOs of the Cl–Cl bridging ligand (symmetry-adapted to interact with the degenerate singly occupied in- and out-of-phase combinations of the Cu d orbitals), most bond lengths (Cu–N = 2.0 Å, Cu–Cl = 2.30 Å, and N–H = 1.09 Å) of the model system were fixed as $\phi$ and $R$ were varied from 85° to 105° and 2.20 to 3.50 Å, respectively. However, for the study of the $\omega$, $R$ dependence of the $e_A - e_O = \delta$ difference, the Cu–Cl and $R$ bond lengths were fixed at 2.30 and 2.84 Å (the latter being the corresponding mean experimental value), respectively; still, the $\omega$ and $\phi$ values were varied from 90° to 120° and 80° to 115°, respectively, and, hence, the $\phi/R$ values were varied from 28 to 40 deg Å$^{-1}$.  

\begin{table}
\centering
\caption{Structural and magnetic data of structurally characterized bis(μ-chloro) copper(II) dimers $^a$}
\begin{tabular}{llllllll}
\hline
Numbering & Complex$^b$ & $2J$ (cm$^{-1}$) & $R$ (Å) & Cu–Cl (Å) & $\phi$ (deg) & $\phi/R$ (deg Å$^{-1}$) & $\omega$ (deg) & Type$^d$ & Reference \\
\hline
1 & $\text{[Cu}_2\text{Cl}_4\text{L}_2\text{]}$ & 4.9 & 2.84 & 2.27 & 96.7 & 34.0 & n.a.$^e$ & I & [52] \\
2 & $\text{[Cu}_2\text{Cl}_4\text{(dmgH)}_2\text{]}$ & 6.3 & 2.70 & 2.24 & 88.0 & 32.6 & 88.0 & I & [18,32,53] \\
3 & $\text{[Cu}_2\text{Cl}_4\text{(Mebta)}_4\text{]}$ (I) & 6.7 & 2.63 & 2.30 & 88.1 & 33.5 & 90.1 & I & this work \\
4 & $\text{[Cu}_2\text{Cl}_4\text{(men)}_2\text{]}$ & -2.1 & 2.73 & 2.31 & 86.1 & 31.5 & 84.1 & I & [31] \\
5 & $\text{[Cu}_2\text{Cl}_4\text{(Pypep)}_2\text{]}$ & -4.6 & 2.83 & 2.32 & 91.1 & 32.2 & 91.5 & I & [54] \\
6 & $\text{[Cu}_2\text{Cl}_4\text{(men)}_2\text{]}$ & -5.6 & 3.15 & 2.26 & 96.8 & 30.8 & 85.3 & I & [55] \\
7 & $\text{[Cu}_2\text{Cl}_4\text{(terpy)}_2\text{]}$ & -5.9 & 2.72 & 2.22 & 90.1 & 33.0 & 81.0 & I & [56] \\
8 & $\text{[Cu}_2\text{Cl}_4\text{(2-pic)}_2\text{]}$ & -7.4 & 3.36 & 2.29 & 100.6 & 29.9 & 94.0 & I & [32] \\
9 & $\text{[Cu}_2\text{Cl}_4\text{(L–L)}_2\text{]}$ & -10.0 & 2.47 & 2.27 & 95.7 & 38.7 & 79.7 & I & [33] \\
10 & $\text{[Cu}_2\text{Cl}_4\text{(Et}_3\text{en)}_2\text{]}$ & 0.1 & 2.73 & 2.28 & 94.8 & 34.8 & 111.0 & II & [18] \\
11 & $\text{[Cu}_2\text{Cl}_4\text{(L’H)}_2\text{]}$ & 5.8 & 2.62 & 2.40 & 89.0 & 33.9 & 124.4 & II & [57] \\
12 & $\text{[Cu}_2\text{Cl}_4\text{(Mebta)}_4\text{]}^{2+}$ (S) & 10.4 & 2.55 & 2.33 & 92.9 & 36.4 & 94.5 & II & this work \\
13 & $\text{[Cu}_2\text{Cl}_4\text{(L–L)}_2\text{]}$ & -14.6 & 2.70 & 2.32 & 95.2 & 35.2 & 118.3 & II & [58,60] \\
14 & $\text{[Cu}_2\text{Cl}_4\text{(GuH)}_2\text{]}$ & -82.6 & 2.45 & 2.29 & 97.9 & 40.0 & 114.0 & II & [18,59] \\
\hline
\end{tabular}
\begin{flushleft}
\textit{a} See text and Scheme 2 for definition of the various parameters. \\
\textit{b} Abbreviations: dmen, N,N-dimethylethylenediamine; dmgH, dimethylglyoxime; Et$_3$en, N,N',N'-triethylethylenediamine, GuaH, the quaminium cation; L, 2,2-bis(2-pyridyl)-1,3-dioxalone, L–L, 2-(2'-pyridyl)quinoloxaline; L’H, benzimidazole; Mepta, 1-methylbenzotriazole; 2-pic, 2-methylpyridine; Pypep, the monoanion of N-(2-4-imidazolylethyl)pyridine-2-carboxamide; terpy, 2,2',6,2'-terpyridine; tmen, N,N,N',N'-tetraethylethylenediamine.
\\
\textit{c} Not available.
\\
\textit{d} See Scheme 1.
\end{flushleft}
\end{table}
A 3D drawing of the \( u, R \) dependence of \( d \) is shown in Fig. 10; a contour plot of the same dependence is provided in Fig. 11. It is clear from both figures that there is a well-corresponding to the crossover point (\( d = 0 \)), hence to ferromagnetic behaviour – at the \( \varphi \) and \( R \) pair values of 90° and 2.33 Å, respectively. The right part of the contour map exhibits a weak antiferromagnetic character, whereas its upper and lower left parts sharply exhibit its strong antiferromagnetic behaviour.

Moreover, Table 10 gives the experimental magnetic and structural data for some structurally characterized copper(II) dimers of both I and II types (Scheme 1). First, type I complexes are given in ascending order of their exchange parameters (numbering from 1 to 9), and then type II ones also in ascending order of their exchange parameters (numbering from 10 to 14). An inspection of the data presented in Table 10 clearly shows that, for both types I and II complexes, there are three compounds exhibiting weak ferromagnetic interaction.

In Fig. 11, the type I complexes are also shown according to their \((\varphi, R)\)-pair values. It is clear from Fig. 11 that both ferromagnetic complexes with the numbers 2 and 3 (ours 1) [see also Table 10] are arranged closer to the lower \( \delta \) values of the well. Due to its lower \( R \) value (both complexes have practically the same \( \varphi \) value), the latter exhibits stronger ferromagnetism and lies closer to the well than the former. In a subsequent stage, all the rest antiferromagnetic type I complexes given in Table 10 are displayed according to their \((\varphi, R)\) values. They are spread to the right of the previous complexes, corresponding to areas of the well with medium \( \delta \) values. All these, in turn, further verify the significance of the two structural parameters \( \varphi \) and \( R \) in the enhancement of both ferromagnetic and antiferromagnetic interactions, and make them our favourite parameters for the establishment of a magnetostructural criterion.

According to Fig. 11, one should expect that ferromagnetic interactions do occur close to the well of the figure, while antiferromagnetic ones do occur at areas on the right side exhibiting higher \( \delta \) values. It is worthwhile mentioning at this point that the criterion just derived holds for neutral, type I \( \text{Cu}(\mu-\text{Cl})_2\text{Cu} \) moiety configurations involving two \( \text{CuN}_2\text{Cl}_3 \) square pyramids with parallel \( \text{CuN}_2(\mu-\text{Cl})\text{Cl} \) bases. However, Fig. 11 in conjunction with values in Table 10 also shows that, with the only exception of complex 1, the criterion holds for type I complexes irrespective of the type of their coordination sphere (\( \text{CuN}_2\text{Cl}_3 \) and/or \( \text{CuN}_3\text{Cl}_2 \)).

A 3D drawing of the \( \omega, \varphi \) dependence of \( d \) is shown in Fig. 12; a contour plot of the same dependence is provided in Fig. 13. It becomes clear from both figures that there is a valley, the well of which – corresponding to the crossover point (\( \delta = 0 \)), hence to ferromagnetic
behaviour – corresponds to the $\omega$ and $\varphi$ pair values of 120° and 90°, respectively; this valley proceeds parallel to the $\omega$ axis. The left part of the contour map strongly exhibits the antiferromagnetic character and this is also the case with the upper right part. The most crucial point emerging from both figures is that the slope of the antiferromagnetic region on the lower right part of the contour plot becomes less sharper upon bending of the $\omega$ angle from 90° to ca. 100°.

In Fig. 13, the type II complexes are also shown according to their ($\omega$, $\varphi$)-pair values. It is clear from Fig. 13 that all three ferromagnetic complexes with the numbers 10, 11 and 12 (ours 5) [see also Table 10] are arranged closer to the lower $\delta$ values of the well than the two antiferromagnetic ones. Complex 11 is not shown in Fig. 13, because it is arranged outside it, in the projection of the valley of the well. However, complex 5 (number 12 in Fig. 13 and Table 10) is arranged very close to the well. Both antiferromagnetic complexes 13 and 14 are arranged to the right of the three ferromagnetic ones, in areas of the well with the sharper slope of the antiferromagnetic region. All these, in turn, further verify the significance of $\omega$ and $\varphi$ in the enhancement of both ferromagnetic and antiferromagnetic interactions making them serious candidates for the establishment of a magnetostructural criterion. According to Fig. 13, one should expect that ferromagnetic interactions do occur close to the valley of the well of the figure, while antiferromagnetic ones do occur at areas on both left and upper right hill sides exhibiting higher $\delta$ values. It should be stressed at this point that the criterion just derived holds (i) for neutral, type II Cu(μ-Cl)$_2$Cu moiety configurations involving two significantly distorted CuN$_2$Cl$_3$ trigonal bipyramids, and (ii) for type II complexes irrespective of their coordination sphere (CuN$_2$Cl$_3$, CuN$_3$Cl$_2$, CuNCl$_4$, and CuCl$_3$) and their total charge.

Contrary to complexes 1 and 5, complex 3 consists of well-separated linear chains possessing alternating square planar Cu(1)Cl$_4$ and trans octahedral Cu(2)Cl$_4$N$_2$ chromophores. The magnetic orbital in the former is a d-type orbital pointing towards the four nearest neighbours, i.e., four chloro ligands. This magnetic orbital is almost perpendicular to that centred on Cu(2) [dihedral angle of 89.4°]. However, the latter magnetic orbital, due to the four identical Cu(2)–Cl bond distances [2.534(1) Å] and the two identical, significantly shorter Cu(2)–N(3) bond distances [1.986(2) Å], could be either one of the two perpendicular (to each other) d-type orbital in the Cu(2)Cl$_2$N(3) planes, see Scheme 3. Hence, the two sequential magnetic orbitals of Cu(1) and Cu(2) along each chain are accidentally orthogonal [51] to each other. This could account well for the ferromagnetic exchange interaction found experimentally.
4. Conclusions

Our systematic investigation of the CuCl₂/Mebta reaction system has confirmed our belief that a variety of complexes with interesting structures and properties are capable of existence. Suitable preparative procedures have now been developed, and the precise identity of the products has been shown to be dependent on the Cu⁺:Mebta reaction ratio, the nature of the solvent and the absence/presence of counterions in the reaction systems. Such considerations will be important as this work is extended to other benzotriazole ligands.

It is interesting to compare the CuCl₂/Mebta and CuBr₂/Mebta [3] reaction systems. Although we do not claim that the synthetic investigations of these systems are complete, it seems that (i) for compounds [CuX₂(Mebta)₂] and (possibly) the 1:1 CuX₂/Mebta complexes, the structures remain unchanged by halide substitution, (ii) complexes [Cu₂Cl₄(Mebta)₄](I), [Cu₂OCl₆(Mebta)₄]·0.25H₂O (4·0.25H₂O) and [Cu₂Cl₄(Mebta)₆]·(ClO₄)₂ (5) have no known counterparts in CuBr₂/Mebta chemistry, and (iii) the mononuclear 1:3 bromo complex [CuBr₂(Mebta)₃] [3] does not have its analogue in CuCl₂/Mebta chemistry. Electronic factors may be responsible for (ii) and (iii).

From the molecular magnetism viewpoint, complexes 1, 3 and 5 are interesting because they exhibit intramolecular (1,5) and intrachain (3) ferromagnetic exchange interactions. We also believe that an important contribution of this work is the fact that insight concerning the effect of structural parameters on the sign and magnitude of the magnetic exchange interactions in 1 and 5 was gained through EHMO calculations performed on a model system. Calculations have permitted the establishment of a new criterion, holding for the magneto-structural correlations in bis(μ-chloro) copper(II) dimers.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 237022(1), 237023(2), 237024(3), 237025(4·0.25H₂O) and 237026(5). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or (www.ccdc.cam.ac.uk)).

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