Copper(II) Chloride–1-Methylbenzotriazole Chemistry: Variation of Product as a Function of Metal-to-Ligand Reaction Ratio; Synthesis, Structure and Properties of a Dinuclear Complex and a Novel Chain Polymer with Two Alternating Chromophores

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The 1:2 and 1:1 reactions of $CuCl_2$ with 1-methylbenzotriazole in EtOH–$CH(OEt)_3$ gave the doubly chloro-bridged dimer $[Cu_2Cl_4(C_7H_7N_3)_4]$ **1** and the novel alternating linear-chain polymer $[\{Cu_2Cl_4(C_7H_7N_3)_2\}_n]$ **2** respectively, crystal structures of which have been determined; magnetic susceptibility studies show that complex **1** possesses intramolecular- and complex **2** intrachain-ferromagnetic coupling.

Several groups have been exploring the co-ordination chemistry of benzotriazoles,[1–6] which is chiefly motivated by the anticorrosion properties of benzotriazole and substituted benzotriazoles towards certain metals, particularly copper and its alloys.[7,8] Moreover, 3d-metal benzotriazolate clusters encompass a range of interesting structural types[1,3,9] and frequently possess unusual magnetic and EPR properties.[4,9–12] For $CuCl_2$ and 1-methylbenzotriazole our studies show that a wide variety of different structures can be accessed through subtle changes in reaction conditions. Here we describe the identity of the products obtained from the $CuCl_2$–$C_7H_7N_3$ reaction mixture in anhydrous EtOH in the absence of added counter ions.

The complexes $[Cu_2Cl_4(C_7H_7N_3)_4]$ **1** and $[\{Cu_2Cl_4(C_7H_7N_3)_2\}_n]$ **2** were prepared† by the reaction of $CuCl_2$ and $C_7H_7N_3$ in EtOH–$CH(OEt)_3$ employing 1:2 and 1:1 mole ratios, respectively. Complex **2** was also isolated in pure form from the solid-state endothermic reaction (1). Powders of empirical formulae $CuCl_2(C_7H_7N_3)_2$ and $CuCl_2(C_7H_7N_3)$ have been known since 1983 when Reedijk *et al.*[13] isolated them from the reactions of 1-methylbenzotriazole with $CuCl_2{\cdot}2H_2O$ in ethanol–*n*-pentane. The authors proposed a halogen-bridged linear-chain structure with two monodentate ligands per Cu^{II} for the 1:2 complex, and suggested a bidentate bridging mode of $C_7H_7N_3$ in the 1:1 compound.

$$\underset{\mathbf{1}}{n[Cu_2Cl_4(C_7H_7N_3)_4]} \xrightarrow[N_2]{152\text{–}203\ ^{\circ}C} \underset{\mathbf{2}}{[Cu_2Cl_4(C_7H_7N_3)_2]_n} + 2nC_7H_7N_3 \uparrow \quad (1)$$

The crystal structure of **1** (Fig. 1) consists of isolated dinuclear molecules with two bridging chloro ligands; a terminal chloride and two nitrogen atoms from two *trans*-$C_7H_7N_3$ ligands complete five-co-ordination at each metal. The bridging Cu_2Cl_2 unit is strictly planar, with a crystallographic inversion centre in the middle of the dimer. The geometry at each copper centre is square pyramidal with the basal plane comprising the two *trans*-nitrogen atoms and two *trans*-chloride ions; the apical site is occupied by the chloride ion which is basal to the other copper 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 the longer, as expected. The Cu $\cdots$ Cu′ separation, the out-of-plane Cu–Cl(1′) distance and the bridging Cu–Cl(1)–Cu′ angle in this complex are all towards the low end of the respective ranges observed for other, structurally similar tetragonal-pyramidal dichloro-bridged copper(II) dimers.[15,16] The $C_7H_7N_3$ groups 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

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† Compound **1**: to a stirred green solution of $CuCl_2$ (0.13 g, 1.0 mmol) in EtOH (20 cm^3) was added $CH(OEt)_3$ (3–4 cm^3). This was refluxed for 30 min and added to a solution of $C_7H_7N_3$ (0.27 g, 2.0 mmol) in anhydrous EtOH (15 cm^3). The resulting blue-green solution was layered with hexanes Et_2O (1:1) (50 cm^3). Slow mixing yielded sky-blue crystals of **1** suitable for a crystal structure analysis. The crystals were collected by filtration, washed with Et_2O and dried in air; yield *ca.* 45% (Found: C, 42.1; H, 3.40; Cl, 17.4; Cu, 16.8; N, 20.8. $C_{28}H_{28}Cl_4Cu_2N_{12}$ requires C, 42.0; H, 3.50; Cl, 17.7; Cu, 15.9; N, 21.0%). Compound **2**: $CuCl_2$ (0.25 g, 1.9 mmol) and $C_7H_7N_3$ (0.24 g, 1.8 mmol) were dissolved in EtOH (80 cm^3) and $CH(OEt)_3$ (5 cm^3). The undisturbed green solution soon began to deposit well-formed, brown crystals of the product. The flask was stored at ambient temperature for 2 d, and the crystals (some were large enough for X-ray crystallography) were filtered off, washed with EtOH and Et_2O, and dried *in vacuo* over P_4O_{10}; yield *ca.* 80% (Found: C, 31.4; H, 2.70; Cl, 27.0; Cu, 24.3; N, 15.4. $C_{14}H_{14}Cl_4Cu_2N_6$ requires C, 31.4; H, 2.60; Cl, 26.5; Cu, 23.7; N, 15.70%).

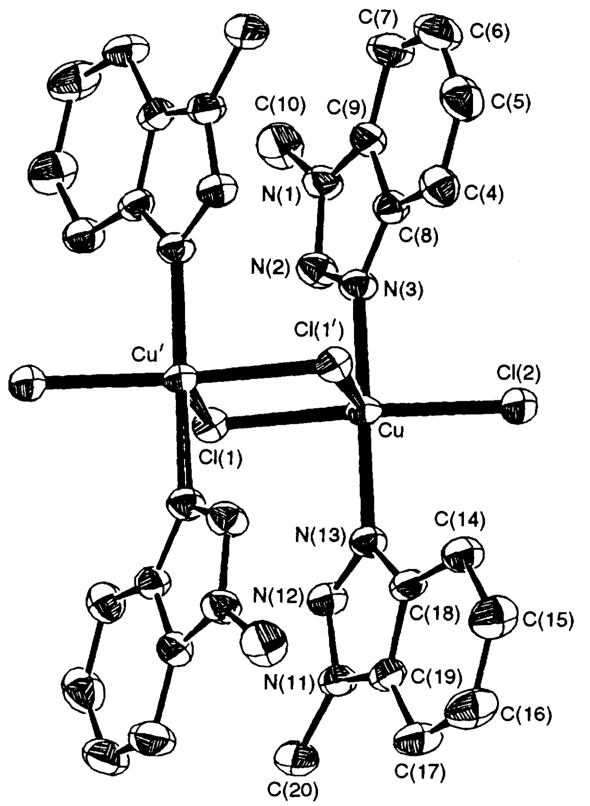

Fig. 1 An ORTEP[14] representation of complex **1**. Most symmetry-related atoms are not labelled: Cu • • • Cu′ 3.438(1), Cu–Cl(1) 2.302(1), Cu–Cl(1′), 2.629(1), Cu–Cl(2) 2.273(1), Cu–N(3) 2.019(2), Cu–N(13) 2.023(1), N(1)–N(2) 1.337(2), N(2)–N(3) 1.317(2) Å; Cu–Cl(1)–Cu′ 88.1(1), Cl(1′)–Cu–Cl(1) 91.9(1), Cl(1′)–Cu–Cl(2) 100.5(1), Cl(1′)–Cu–N(3) 94.3(1), Cl(1′)–Cu–N(13) 93.2(1), Cl(1)– Cu–Cl(2) 167.6(1), Cl(1)–Cu–N(3) 89.0(1), Cl(1)–Cu–N(13) 89.2(1), Cl(2)–Cu–N(3) 90.1(1), Cl(2)–Cu–N(13) 90.1(1), N(3)–Cu–N(13) 172.3(1)°

N(1)N(2)N(3)C(8)C(4)C(5)C(6)C(7)C(9) mean plane is 3.50 Å for N(12′)].‡

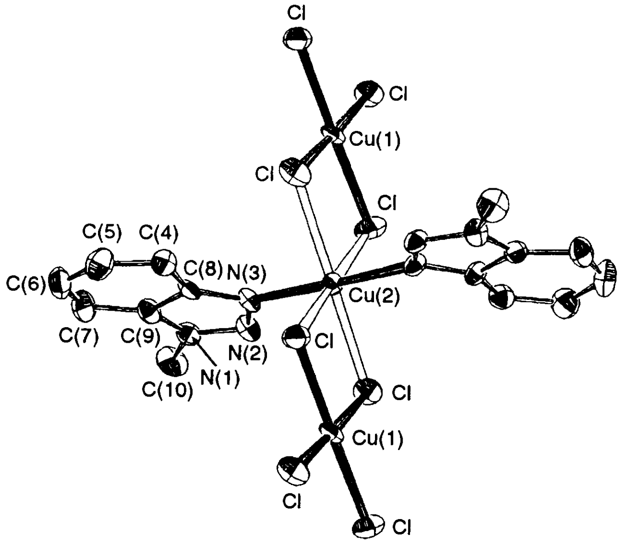

Fig. 2 An ORTEP representation of a part of complex **2**. Symmetry-related carbon and nitrogen atoms are not labelled: Cu(1) • • • Cu(2) 3.556(1), Cu(1)–Cl 2.260(1), Cu(2)–Cl 2.535(1), Cu(2)–N(3) 1.986(2), N(1)–N(2) 1.335(3), N(2)–N(3) 1.313(3) Å; Cu(2)–Cl–Cu(1) 95.6(1), Cl–Cu(1)–Cl 90.4(1), Cl–Cu(2)–Cl 78.5(1), Cl–Cu(2)–N(3) 89.4(1), N(1)–N(2)–N(3) 108.0(2)°

The crystal structure‡ of **2** (Fig. 2) is composed of linear, well-separated polymeric chains of Cu^{II} atoms bridged asymmetrically by two chloro ligands. A regular alternation of two non-equivalent copper atoms [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 *trans*-octahedral $(\mu\text{-Cl})_4N_2$ environment. There is a mirror plane through Cu(2) and the $C_7H_7N_3$ ligands and a second one, parallel to the first, through Cu(1), and a two-fold 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 Cu(1)–Cl bond distance [2.260(1) Å] is noticeably shorter than the Cu(2)–Cl bond length [2.535(1) Å], consistent with the lower co-ordination number for Cu(1). The doubly-bridged chain with two alternating chomophores observed in **1** is unique for complexes of the formulation CuX_2L (X = Cl or Br, L = monodentate ligand) as far as we are aware.[20]

Variable-temperature magnetic susceptibility data were collected for powdered samples of **1** and **2** in the temperature range 4.2–294 K. For complex **1**, the effective magnetic moment, μ_{eff}, per Cu^{II} rises from 1.83 at 294 to 1.91 μ_B ($\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}) at 4.2 K, which, together with the positive Weiss constant, is consistent with ferromagnetic coupling. Small anomalies for the $\chi_M^{-1} = f(T)$ relation were observed in the lowest temperature range only. Hence, the experimental data between 4.2 and 20.0 K have been fitted to the Bleaney–Bowers equation[21] with a molecular-field correction[22,23] [spin Hamiltonian $\hat{\mathscr{H}} = -2J(\hat{S}_A \cdot \hat{S}_B) + g\beta H\hat{S}$, $\hat{S}$ is the total spin operator $\hat{S} = \hat{S}_A + \hat{S}_B$]. The best fitting parameters obtained are $2J = +7$ cm^{-1} and $zJ' = -1.1$ cm^{-1} (J' and z are the interdimer exchange parameter and the number of the nearest neighbouring dimers in the crystal lattice, respectively) by minimizing the function R [equation (2)] to 4.46×10^{-3}.

$$[R = \sum_{i=1}^{n} (\chi_i^{expt} - \chi_i^{calc})^2/(\chi_i^{expt})^2] \qquad (2)$$

For **2**, the product $\chi_M T$ increases upon cooling, reaches a maximum (0.625 cm^3 K mol^{-1}) at *ca.* 21 K and then decreases to 0.563 cm^3 K mol^{-1} at 4.3 K. Taking into account the crystal structure of this complex (see above), the magnetic data were

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‡ Crystal data. $C_{28}H_{28}Cl_4Cu_2N_{12}$ **1**, $M = 801.51$, monoclinic, space group $P2_1/n$, $a = 9.927(1)$, $b = 15.627(1)$, $c = 10.753(1)$ Å, $\beta = 96.69(1)°$, $U = 1656.71$ Å^3, $Z = 2$, $F(000) = 812$, $D_c = 1.61$ g cm^{-3}, $T = 296$ K, $\mu = 15.71$ cm^{-1}, 3938 reflections measured, 3600 unique, giving 3012 with $F_o > 6.0\sigma(F_o)$ [$R_{int} = 0.0201$], 264 refined parameters, $[\Delta/\sigma]_{max} = 0.012$, $[\Delta\rho]_{max}$, $[\Delta\rho]_{min} = 0.299, -0.322$ e Å^{-3}, R ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) = 0.0242 ($R'$ $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ = 0.0407) for 3012 independent observed reflections, $w = 1/[\sigma^2(F_o) + 0.0003F_o^2]$.

$C_{14}H_{14}Cl_4Cu_2N_6$ **2**, $M = 535.20$, monoclinic, space group $I2/m$, $a = 8.877(1)$, $b = 7.112(1)$, $c = 14.876(1)$ Å, $\beta = 93.94(1)°$, $U = 937.03$ Å^3, $Z = 2$, $F(000) = 532$, $D_c = 1.90$ g cm^{-3}, $T = 296$ K, $\mu = 28.60$ cm^{-1}, 1134 reflections measured, 1093 unique, giving 1011 with $F_o > 4.0\sigma(F_o)$[$R_{int} = 0.0141$], 97 refined parameters, $[\Delta/\sigma]_{max} = 0.045$, $[\Delta\rho]_{max}$, $[\Delta\rho]_{min} = 0.342, -0.253$ e Å^{-3}, $R = 0.0204$, ($R' = 0.0215$) for 1011 independent observed reflections, unit weights.

For both compounds unit-cell dimensions derived from a least-squares refinement of the setting angles of 25 automatically centred reflections ($11 < 2\theta < 23°$) on a Nicolet $P2_1$ diffractometer upgraded by CRYSTAL LOGIC[17] with zirconium-filtered Mo-Kα radiation. Intensity data recorded using a θ–2θ scan method to $2\theta_{max} = 54°$, with scan speed 4.5° min^{-1} (**1**) and 3.0° min^{-1} (**2**), and scan width 2.5° (**1**) and 2.7° (**2**) plus $\alpha_1\alpha_2$ separation. Lorentz, polarization and ψ-scan absorption corrections applied. Structures solved by direct methods using SHELX 86[18] and refined by full-matrix least-squares techniques (SHELX 76[19]). Non-hydrogen atoms refined with anisotropic thermal parameters. All hydrogen atoms located by difference maps and their positions refined isotropically. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

fitted by the Heisenberg model of the magnetic interaction (Padé expansion series[24–26] for $S = \frac{1}{2}$) assuming a first-order molecular-field correction to account for the interchain interactions. The best fitting parameters obtained are $J = +15.7$ cm^{-1} and $zJ' = -4.0$ cm^{-1} with $R = 2.05 \times 10^{-1}$. Hence, for $z = 4$ $J_{\text{inter}} = -1$ cm^{-1} and $J_{\text{inter}}/J_{\text{intra}} = \frac{1}{16}$. Consequently, complex **2** constitutes a very interesting example of a molecular ferromagnet in which one-dimensional chains are coupled antiferromagnetically.

The monodentate co-ordination of $C_7H_7N_3$, observed even in the 1 : 1 complex **2** may in part account for the lack of long-term corrosion inhibition on copper by 1-methylbenzotriazole.[27] Further detailed studies of **1** and **2** are in progress, and additional $CuCl_2$–$C_7H_7N_3$ species—including high nuclearity clusters—are under investigation.

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