Synthesis and X-ray crystal structure of a novel neutral trinuclear copper(ii) hydridotris(3,5-dimethylpyrazolyl)borate complex with 1,1-azido bridges

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The X-ray crystal structure and magnetic properties of a neutral trinuclear 1,1-azido bridged copper(II) complex [LCu(μ-N_3)$_2$Cu(μ-N_3)$_2$CuL] 2 [L = hydridotris(3,5-dimethylpyrazolyl)borate], produced from the reaction between [Cu_3L_2]Cl 1 and an excess of trimethylsilyl azide, are reported.

Recent interest in copper hydridotris(pyrazolyl)borate complexes has been aroused by its resemblance to active sites in some copper-containing metalloproteins[1] and their catalytic properties towards cyclopropanation and aziridination.[2] In this work, we report the reaction between [Cu_3L_2]Cl **1**† and trimethylsilyl azide in polar solvents such as acetone and methanol which gives a neutral trinuclear copper(ii) hydridotris(3,5-dimethylpyrazolyl)borate complex, [LCu(μ-N_3)$_2$Cu(μ-N_3)$_2$CuL] **2**,‡ containing four 1,1-azido bridges. To the best of our knowledge, with the exception of one structure containing an infinite chain of Cu^{II}–N_3 units[3] and a recently reported hexanuclear copper(ii) complex with 1,3-azides,[4] all reported copper(ii)–μ-azido systems were binuclear.[5]

Complex **1** is obtained by slow addition of 0.5 equiv. of ligand KL to a suspension of copper(i) chloride in acetone. Such an approach is adopted in order to prevent formation of a copper(i)–polypyrazolylborate dimer.[6] The pink–white solid **1** is air-stable but its dichloromethane solution is air-sensitive. FABMS of **1** (noba matrix) gives the highest mass ion at *m/z* 785. This suggests that **1** possesses an oligomeric structure of two L ligands and three Cu metal ions. A trinuclear structure (Fig. 1) is proposed in which each Cu^I is coordinated to two 3,5-dimethylpyrazolyl units from two L ligands. ^{1}H NMR (300 MHz, CD_2Cl_2) of **1** supports the proposed structure. Three sets of protons in 3 : 3 : 1 ratio are observed which can be assigned as follows: δ 1.65 (s, 18 H, pyrazolyl-CH_3), 2.42 (s, 18 H, pyrazolyl-CH_3) and 5.92 (s, 6 H, pyrazolyl-H). To the best of our knowledge, complex **1** represents a new mode of coordination for the well studied copper(ii)–polypyrazolylborate system.

Complex **2** is obtained by the addition of trimethylsilyl azide to a suspension of **1** in a polar solvent such as acetone or methanol. The ν(B–H) stretch of L in complexes **1** and **2** is observed at 2526 and 2528 cm^{-1}, respectively. The asymmetric ν(N_3) stretch of **2** is found at 2075 cm^{-1} which is consistent with the presence of 1,1-bridging azides. The structure of **2** is shown in Fig. 2.§ The structure contains a square-planar central Cu^{II} and two distorted square-pyramidal terminal Cu^{II} atoms. The molecule is centrosymmetric with only half of the molecule crystallographically independent. The hydridotris(3,5-dimethylpyrazol-1-yl)borate acts as a tripodal ligand coordinating to the terminal Cu^{II} with bond distances and angles (1.96–2.18 Å, 86.9–92.0°) comparable to known copper(i) polypyrazolylborate complexes.[1f,g,6] The three Cu^{II} atoms are bridged by four 1,1-azides with a Cu^{II}–N(azido) average distance of 1.99 Å. The average Cu–N(azido)–Cu angle is 101.4° and are typical for the 1,1-azido copper moiety.[5a,c] The μ-azides are considered symmetrical with N–N bond distances of 1.15(2)–1.20(2) Å. The N–N–N angles are all 179.0(3)°. The average Cu···Cu distance is 3.05 Å.

It is known that magnetic orbital interactions between the Cu^{II} ions in many binuclear 1,1-azido systems result in ferromagnetic coupling.[5a,c] However, this is not observed in our trinuclear system (Fig. 3). The $\chi_M T$ is found to be independent of temperature throughout the temperature range of 75.5–300 K. The χ_M^{-1} *vs.* *T* variation of **2** shows typical Curie–Weiss behaviour with a Curie constant of 1.34 cm^3 K mol^{-1} and a Weiss temperature, θ, of −0.20 K. The μ_{eff} of **2** within the

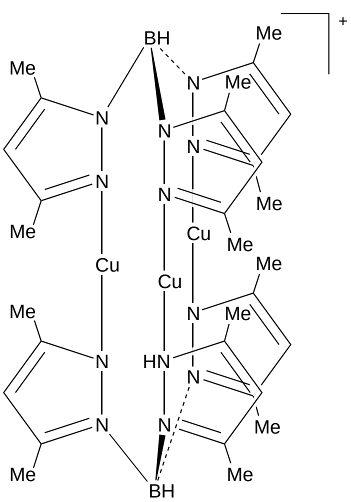

Fig. 1 The proposed structure of **1**

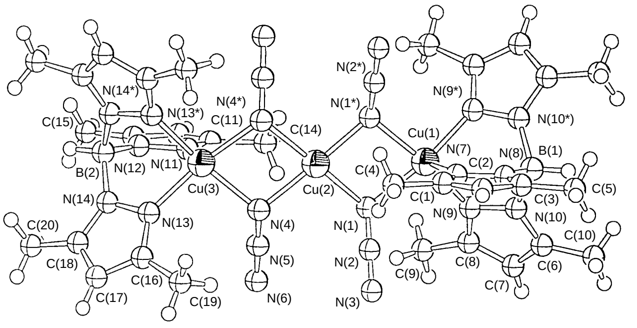

Fig. 2 Perspective view of [LCu(μ-N_3)$_2$Cu(μ-N_3)$_2$CuL] **2**. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.03(1), Cu(1)–N(7) 2.15(2), Cu(1)–N(9) 1.96(1), Cu(2)–N(1) 1.95(1), Cu(2)–N(4) 1.96(1), Cu(3)–N(4) 2.00(1), Cu(3)–N(11) 2.18(2), Cu(3)–N(13) 1.96(1), N(1)–N(2) 1.20(2), N(2)–N(3) 1.15(2), N(4)–N(5) 1.18(2), N(5)–N(6) 1.17(2), Cu(1)···Cu(2) 3.082(3), Cu(2)···Cu(3) 3.63(3); N(1)–Cu(1)–N(1*) 76.2(8), N(7)–Cu(1)–N(9) 92.0(5), N(9)–Cu(1)–N(9*) 86.9(7), N(1)–Cu(2)–N(4) 101.0(5), N(1)–Cu(2)–N(4*) 177.5(7), N(4)–Cu(3)–N(4*) 76.2(7), N(11)–Cu(3)–N(13) 91.9(4), N(13)–Cu(3)–N(13*) 87.6(7), Cu(1)–N(1)–Cu(2) 101.5(6), Cu(2)–N(4)–Cu(3) 101.2(6), N(1)–N(2)–N(3) 179(3), N(4)–N(5)–N(6) 179(2).

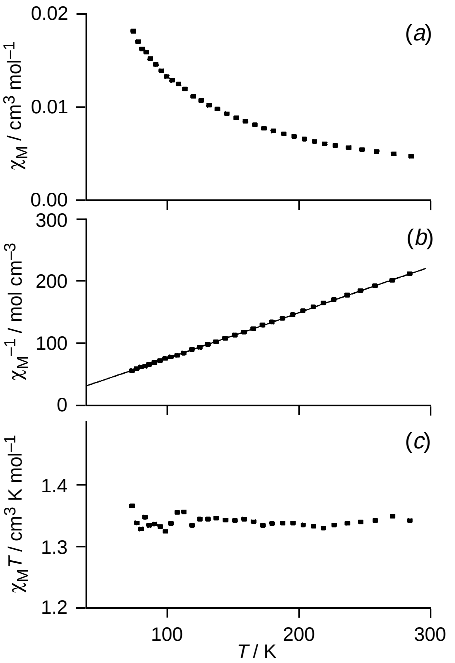

Fig. 3 Magnetic properties of **2**: (*a*) temperature dependence of χ_M; (*b*) χ_M^{-1} *vs. T*, the solid line is the best fit for the Curie–Weiss behaviour, $\chi = C/(T - \theta)$, with $C = 1.34$ cm^3 K mol^{-1} and $\theta = -0.20$ K; (*c*) temperature dependence of the product $\chi_M T$

above temperature range is found to be fairly constant at *ca.* 3.3 μ_B. These indicate a weak antiferromagnetic coupling[5e,7] among adjacent Cu^{II} centres in **2**. The magnetic properties of this trinuclear 1,1-azido bridged copper(ii) system will be further studied.

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Footnotes

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† **1** was synthesized by slow addition of an acetone solution of potassium tris(3,5-dimethylpyrazolyl)borohydride (0.5 equiv.) to a suspension of copper(i) chloride in acetone under a nitrogen atmosphere. The resultant pink–white suspension was allowed to stir at room temp. in darkness under a nitrogen atmosphere for 12 h. The crude product of **1** was collected by filtration and was washed with diethyl ether. Yield 60%. IR (cm^{-1}): 2526 ν(B–H). ^{1}H NMR (300 MHz, CD_2Cl_2) and FABMS (NOBA matrix) data: see text. The crude product was used in subsequent synthesis without further purification.

‡ **2** was synthesized by addition of 0.45 g of trimethylsilyl azide to a suspension of 0.50 g of **1** in 20 ml methanol in open atmosphere. The suspension immediately turned yellow–green. Further stirring at room temp. (8 h) yielded a green–brown precipitation of crude **2** which was collected by filtration and washed with diethyl ether. Yield 35%. X-Ray quality crystals of **2** were obtained by slow diffusion of diethyl ether into a dichloromethane solution. IR (cm^{-1}): 2522 ν(B–H), 2075 ν(N_3). Satisfactory elemental analysis.

§ *Crystal data*; $C_{30}H_{52}B_2Cu_3N_{24}$ **2**, $M = 961.16$, monoclinic, space group $P2_1/m$ (no. 11), $T = 296$ K, $a = 8.036(2)$, $b = 13.232(3)$, $c = 23.407$ Å, $\beta = 94.41(1)°$, $U = 2481.7(7)$ Å^3, crystal size 0.22 × 0.23 × 0.33 mm, $Z = 2$, $D_c = 1.286$ g cm^{-3}, $F(000) = 994.00$, graphite monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 13.22$ cm^{-1}, of 3711 reflections, 3428 were unique with $R_{int} = 0.058$; the structure was solved by Patterson methods (DIRDIF92 PATTY) and refined by full-matrix least squares, function minimized: $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\delta_c^2(F_o) + (p^2/4)(F_o)^2]^{-1}$, residuals: $R = 0.054$, $R_w = 0.056$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/441.

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