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Three new dinuclear copper(II) complexes with $[Cu(\mu_{1,3}\text{-}N_3)_2Cu]^{2+}$ and $[Cu(\mu_{1,1}\text{-}N_3)_2Cu]^{2+}$ asymmetrical cores: syntheses, structures and magnetic behaviour

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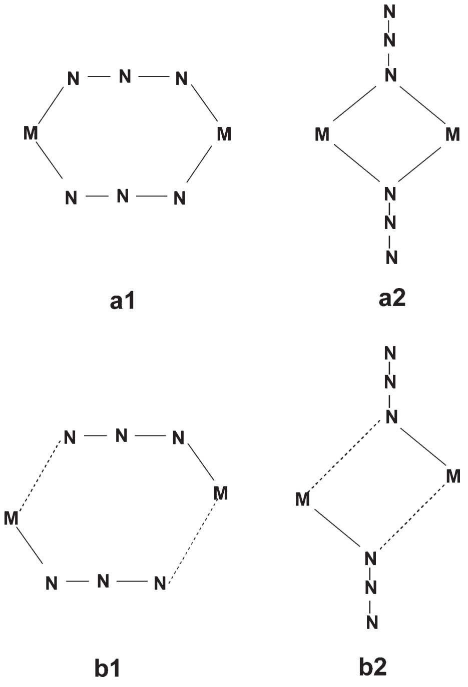
Three new dinuclear copper(II) complexes, derived from end-to-end and end-on azido bridging ligands and triamine derivatives, have been synthesized and their crystal structures have been determined by X-ray diffraction methods. These are the dinuclear end-to-end compounds, $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2](ClO_4)_2$ (**1**) and $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2](ClO_4)_2$ (**2**), and the dinuclear end-on compound $[Cu_2(\mu_{1,1}\text{-}N_3)_2(Medien)_2](ClO_4)_2$ (**3**) (Et$_3$dien is triethyldiethylenetriamine, Medpt is methyldipropylenetriamine and Medien is methyldiethylenetriamine). The $[Cu(\mu\text{-}N_3)_2Cu]^{2+}$ cores are asymmetrical in all 3 compounds. Variable temperature magnetic susceptibility data were collected and fitted to the appropriate equation derived from the Hamiltonian $H = -JS_1S_2$. **1** shows unusual ferromagnetic interactions with $J = 9$ cm^{-1} through the end-to-end azido bridges while **2** shows an antiferromagnetic interaction through the end-to-end azido bridges with the highest reported absolute magnitude of $J = -105$ cm^{-1}. The magnetic data of **1** and **2** have been correlated with the Addison parameter, τ, and mainly with the Cu–N$_3$–Cu torsion angle, Δ. **3** shows an unusual antiferromagnetic interaction with $J = -16.8$ cm^{-1} through the end-on azido bridges.

Introduction

Dinuclear copper(II) azide-bridged systems have received considerable attention in recent years due to their broad range of structural and magnetic properties, which are a good test for theoretical analysis of the exchange coupling.[1–5] The azide ligand acts as a bridge between copper(II) atoms in two principal ways: the $\mu_{1,3}$ (end-to-end) mode (a1 and b1 in Scheme 1) *via* both of the peripheral nitrogen donor atoms and the $\mu_{1,1}$ (end-on) mode (a2 and b2 in Scheme 1) *via* one nitrogen donor. The first coordination mode usually gives rise to antiferromagnetic (AF) coupling whereas the second coordination mode usually gives rise to ferromagnetic (F) coupling. Centring our attention on the dinuclear doubly-bridged azido copper(II) compounds structurally and magnetically studied, two main possibilities are found. (1) Compounds with four short Cu–N(azide) distances (symmetrical doubly-bridged azido copper(II) complexes), which are strongly AF coupled[6] in the case of the end-to-end coordination mode a1 or strongly F coupled[2,7–13] in the case of the end-on coordination mode a2. (2) Compounds with two short and two long Cu–N(azide) distances (asymmetrical doubly-bridged azido copper(II) complexes), which are usually weakly AF coupled[4,12,14–17] in the case of the end-to-end coordination mode b1 or weakly F coupled[17–22] in the case of the end-on coordination mode b2.

The asymmetrical doubly-bridged azido copper(II) complexes are usually pentacoordinate and the geometry around the



Scheme 1

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copper(II) atom is usually intermediate between square pyramid and trigonal bipyramid. Each geometry implies a different admixture of the $d_{x^2-y^2}$ and d_{z^2} orbitals for the resulting magnetic orbitals in the dinuclear complexes and, consequently, a different superexchange interaction and different J coupling constants. In the asymmetrical doubly-bridged azido copper(II) complexes with the end-to-end coordination mode, some attempts to correlate the structural parameters with the J values have been made[4,14,16] but the results are far from being definitive, due in part to the low number of structurally and magnetically studied compounds.[16] In the asymmetrical doubly-bridged azido copper(II) complexes with the end-on coordination mode, as far as we know, no attempts to correlate the structural parameters with the J values have been made. The asymmetrical doubly-bridged azido copper(II) complexes with the end-to-end or end-on coordination modes have another peculiarity: the coordination mode does not determine the magnetic coupling (F or AF) as it is found for the symmetrical doubly-bridged azido copper(II) complexes. In this paper we report three new asymmetrical doubly-bridged azido copper(II) complexes, two of them with the end-to-end coordination mode, $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2](ClO_4)_2$ (**1**) and $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2](ClO_4)_2$ (**2**), and the other, $[Cu_2(\mu_{1,1}\text{-}N_3)_2(Medien)_2](ClO_4)_2$ (**3**), with the end-on coordination mode (Et$_3$dien is triethyldiethylenetriamine, Medpt is methyldipropylenetriamine and Medien is methyldiethylenetriamine). Their crystallographic structures and magnetic behaviour are described below.

Experimental

Physical measurements

Infrared spectra were measured on Jasco FT-IR 480 plus and Nicolet 520 FTIR spectrophotometers as KBr pellets. Magnetic susceptibility measurements were carried out on polycrystalline samples with a SQUID apparatus working in the range of 2–300 K under magnetic fields of approximately 0.2 T. Diamagnetic corrections were estimated from Pascal tables.

Syntheses

WARNING! The reported azido complexes are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

$[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2](ClO_4)_2$ (1). **1** was prepared by mixing 3 mmol of copper(II) perchlorate hexahydrate, 3 mmol of triethyldiethylenetriamine and 3 mmol of sodium azide in 50 ml of water. From this solution green monocrystals suitable for X-ray determination were collected two weeks later. Yield: 0.4 g, 34%. $\nu_{as}(N_3)$ 2051 (vs) cm^{-1}. Anal. calcd for $C_{20}H_{50}Cl_2Cu_2N_{12}O_8$: C, 30.6; H, 6.4; N, 21.4; Cl, 9.0; found: C, 30.7; H, 6.6; N, 21.2; Cl, 8.9%.

$[Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2](ClO_4)_2$ (2). Two routes were used to synthesize this complex.

Route a: To a solution containing copper(II) perchlorate hexahydrate (1.85 g, 5 mmol) and methyldipropylenetriamine (0.73 g, 5 mmol) in 15 ml H_2O, NaN_3 (0.65 g, 10 mmol) dissolved in 10 ml H_2O was added drop by drop. The resulting green solution was stirred for 10 min and then left to crystallize at room temperature. The green precipitate that separated out was collected by filtration, washed with 5 ml of cold EtOH, ether and air dried. When the mother liquor was allowed to stand at room temperature more precipitate was obtained. Single crystals suitable for X-ray diffraction measurements were obtained from the mother liquor upon standing at room temperature for 4 days (overall yield: 1.5 g, 86%).

Route b: To a methanolic solution (50 ml) containing copper(II) perchlorate hexahydrate (1.85 g, 5 mmol) and methyldipropylenetriamine (0.73 g, 5 mmol), a hot slurry solution of NaN_3 (0.65 g, 10 mmol) in 100 ml MeOH was added drop by drop. The resulting green solution was quickly filtered, heated on a steam bath for 5 min and then allowed to stand at room temperature. The shiny green crystals that separated out after 1 h were collected by filtration, washed with ether and air dried. Other batches were produced from the mother liquors to give a total yield of 1.6 g (91%). Single crystals were also produced from these solutions.

$\nu_{as}(N_3)$ 2046 (vs) cm^{-1}. Anal. calcd for $C_{14}H_{38}N_{12}Cl_2O_8Cu_2$: C, 24.1; H, 5.5; N, 24.0; found: C, 24.1; H, 5.5; N, 24.0%.

$[Cu_2(\mu_{1,1}\text{-}N_3)_2(Medien)_2](ClO_4)_2$ (3). **3** was prepared by mixing 3 mmol of copper(II) perchlorate hexahydrate, 3 mmol of methyldiethylenetriamine and 3 mmol of sodium azide in 40 ml of water. From this solution green monocrystals suitable for X-ray determination were collected one week later. Yield: 0.5 g, 52%. $\nu_{as}(N_3)$ 2083 (vs) cm^{-1}. Anal. calcd for $C_{10}H_{30}Cl_2Cu_2N_{12}O_8$: C, 18.6; H, 4.7; N, 26.1; found, C 18.7, H, 4.8; N, 26.3%.

Crystal structure analyses

The X-ray single-crystal data for the three compounds were collected on a Phillips PW-1100 for **1** and **3** and on a modified STOE four-circle diffractometer for **2**. Crystal size: **1** [**2** and **3**, respectively] $0.1 \times 0.1 \times 0.2$ mm^3 [$0.12 \times 0.22 \times 0.45$ and $0.40 \times 0.25 \times 0.20$ mm^3]. The crystallographic data, the conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. Graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) with the $\omega/2\theta$ (ω scan and $\omega/2\theta$) technique was used to collect the data sets. The accurate unit cell parameters were determined from automatic centring of 32 reflections ($2° < \theta < 30°$) [56 reflections ($3.5° < \theta < 17.2°$) and 24 reflections ($7.0° < \theta < 14.0°$)] and refined by least-squares methods. A total of 1717 reflections (1652 independent reflections, $R_{int} = 0.068$) [3248 reflections (2684 independent reflections, $R_{int} = 0.026$) and 4361 reflections (3625 independent reflections, $R_{int} = 0.0427$)] were collected in the range $3.5° < \theta < 29.4°$ [$2.8° < \theta < 26.0°$ and $2.77° < \theta < 26.98°$]. Intensity decays of 6% [3% and 3%] for control reflections (−1 4 −1; −1 2 1; 0 4 2) [(−1 1 −1; 0 −2 3) and (1 1 4; −1 −2 −1; 2 2 − 2)], measured after every set of 100 reflections, was observed during data collection. Corrections were applied for Lorentz polarization effects, for intensity decay, and for absorption in the case of **2**, using the DIFABS[23] computer program. The structures were solved by direct methods using the SHELXS-86[24] computer program and refined by full-matrix least-squares methods on F^2, using the SHELXL-93[25] program incorporated in the SHELXTL/PC V 5.03[26] program library and the graphics program PLATON.[27] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were obtained from ΔF maps and subsequently fixed geometrically with the HFIX utility.[26] Final R indices for all observed reflections: 0.0455 [0.0387 and 0.0481]; number of refined parameters: 276 [187 and 243]. Maximum and minimum peaks in the final difference Fourier synthesis: 0.28 and −0.46 e Å^{-3} [0.61 and −0.40 e Å^{-3}; 0.37 and −0.66 e Å^{-3}]. Significant bond parameters are reported in Tables 2, 3 and 4, respectively. †

Results and discussion

Crystal structures

$[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2](ClO_4)_2$ (1). The structure of **1** consists of the dinuclear units $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2]^{2+}$ and

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† CCDC reference numbers 229685–229687. See http://www.rsc.org/suppdata/nj/b3/b314526c/ for crystallographic data in .cif or other electronic format.

Table 1 Crystal data and structure refinement for compounds [Cu$_2$($\mu_{1,3}$-N$_3$)$_2$(Et$_3$dien)$_2$](ClO$_4$)$_2$ (**1**), [Cu$_2$($\mu_{1,3}$-N$_3$)$_2$(Medpt)$_2$](ClO$_4$)$_2$ (**2**) and [Cu$_2$($\mu_{1,1}$-N$_3$)$_2$(Medien)$_2$](ClO$_4$)$_2$ (**3**)

	1	2	3
Chemical formula	$C_{20}H_{50}Cl_2Cu_2N_{12}O_8$	$C_{14}H_{38}Cl_2Cu_2N_{12}O_8$	$C_{10}H_{30}Cl_2Cu_2N_{12}O_8$
Formula weight	784.69	700.56	644.44
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*21/*c*	*P*−1
a/Å	23.638(4)	7.536(2)	8.524(6)
b/Å	11.011(2)	12.597(3)	8.780(4)
c/Å	13.924(3)	14.629(4)	11.320(6)
α/°	90.0	90.0	71.79(5)
β/°	104.65(3)	99.77(2)	68.88(6)
γ/°	90.0	90.0	63.20(5)
U/Å^3	3506(2)	1368.6(6)	693.9(7)
Z	4	2	1
T/°C	20(2)	25(2)	20(2)
μ(Mo Kα)/mm^{-1}	1.423	1.811	1.779
$R(I > 2\sigma(I))$	0.0455	0.0387	0.0481
wR(all data)	0.156	0.1014	0.1587

perchlorate anions. The minimum inter-dinuclear Cu–Cu distance is 7.36(1) Å. The copper(II) atoms are bridged by two azide ions in a $\mu_{1,3}$ end-to-end fashion. An ORTEP drawing with the atom labelling scheme is shown in Fig. 1. The main bond lengths and angles are given in Table 2. The copper atoms are pentacoordinated by the three N atoms of the Et$_3$dien and two azide N atoms (one from each of the two bridging groups). The coordination polyhedron around copper(II) can be described as an axially elongated square planar pyramid. The three Cu-to-amine N(4), N(5) and N(6) distances are 2.024(7), 2.045(5) and 2.049(6) Å, respectively. The bonding of copper to the azido nitrogens N(1) and N(3) is asymmetric with bond lengths of 2.379(7) and 2.099(5) Å. The Cu–N(1)–N(2) and Cu–N(3)–N(2)′ angles in the bridges are 137.8(6)° and 123.8(5)°, respectively. The six atoms of the N$_3$ bridging ligands are in a plane, with the dihedral angle between this plane and the N(1)–Cu–N(3) plane being 18.4(3)°. The intradimer Cu–Cu distance is 5.407(2) Å.

[Cu$_2$($\mu_{1,3}$-N$_3$)$_2$(Medpt)$_2$](ClO$_4$)$_2$ (2). The core structure of **2** is very similar to that of **1**, consisting of the dinuclear units [Cu$_2$($\mu_{1,3}$-N$_3$)$_2$(Medpt)$_2$]$^{2+}$ and perchlorate anions. The minimum inter-dinuclear Cu–Cu distance is 7.536(2) Å. The copper(II) atoms are bridged by two azide ions in a $\mu_{1,3}$ end-to-end fashion. An ORTEP drawing with the atom labelling scheme is shown in Fig. 2. The main bond lengths and angles are given in Table 3. The copper atoms are pentacoordinated by the three N atoms of the Medpt, one N atom of one bridging azide and one N atom of the other bridging azide group. The coordination polyhedron around copper(II) can be described as an axially elongated square planar pyramid. The Cu-to-amine N(1), N(2) and N(3) distances are 1.976(3), 2.075(3) and 1.978(3) Å, respectively. The copper-to-azide Cu–N(11) and Cu–N(13) bond lengths are, as in **1**, dissimilar at 2.093(3) and 2.309(3) Å, respectively. The Cu–N(11)–N(12) and Cu–N(13)–N(12′) angles in the bridge are 122.5(2)° and 139.4(2)°, respectively. The six atoms of the N$_3$ bridging ligands are in a plane; the dihedral angle between this plane and the N(11)–Cu(1)–N(13) plane is 6.0(3)°. The intradimer Cu–Cu distance is 5.302(2) Å.

Table 2 Selected bond lengths (Å) and angles (°) for [Cu$_2$($\mu_{1,3}$-N$_3$)$_2$(Et$_3$dien)$_2$](ClO$_4$)$_2$ (**1**)

Cu–Cu′	5.407(2)	Cu–N(1)	2.379(7)
Cu–N(3)	2.099(5)	Cu–N(4)	2.024(7)
Cu–N(5)	2.045(5)	Cu–N(6)	2.049(6)
N(1)–N(2)	1.148(10)	N(3)–N(2)′	1.196(10)
N(1)–Cu–N(3)	89.3(3)	N(1)–Cu–N(4)	99.7(3)
N(1)–Cu–N(5)	98.9(2)	N(1)–Cu–N(6)	99.5(3)
N(3)–Cu–N(4)	94.8(2)	N(3)–Cu–N(5)	171.7(3)
N(3)–Cu–N(6)	92.0(2)	N(4)–Cu–N(5)	85.2(2)
N(4)–Cu–N(6)	159.7(3)	N(5)–Cu–N(6)	85.4(2)
N(1)–N(2)–N(3)′	176.2(8)	Cu–N(1)–N(2)	137.8(6)
Cu–N(3)–N(2)′	123.8(5)		

[Cu$_2$($\mu_{1,1}$-N$_3$)$_2$(Medien)$_2$](ClO$_4$)$_2$ (3). The structure of **3** consists of the dinuclear [Cu$_2$($\mu_{1,1}$-N$_3$)$_2$(Medien)$_2$]$^{2+}$ units and perchlorate anions. In contrast to **1** and **2**, the copper(II) atoms are bridged by azido ions in an end-on fashion. An ORTEP drawing with the atom labelling scheme is shown in Fig. 3. The main bond lengths and angles are given in Table 4. The copper atoms are pentacoordinated by the three N atoms of the Medien and two azide N atoms from the two bridging azide group. The coordination polyhedron around copper(II) can be described as intermediate between an axially elongated

Table 3 Selected bond lengths (Å) and angles (°) for [Cu$_2$($\mu_{1,3}$-N$_3$)$_2$(Medpt)$_2$](ClO$_4$)$_2$ (**2**)

Cu(1)–Cu(1)′	5.302(2)	Cu(1)–N(1)	1.976(3)
Cu(1)–N(2)	2.075(3)	Cu(1)–N(3)	1.978(3)
Cu(1)–N(11)	2.093(3)	Cu(1)–N(13)	2.309(3)
N(11)–N(12)	1.174(4)	N(12)–N(13)′	1.152(4)
N(1)–Cu(1)–N(2)	91.65(11)	N(1)–Cu(1)–N(11)	86.34(13)
N(1)–Cu(1)–N(13)	90.07(13)	N(2)–Cu(1)–N(3)	94.44(11)
N(2)–Cu(1)–N(11)	156.09(11)	N(2)–Cu(1)–N(13)	109.27(10)
N(3)–Cu(1)–N(11)	84.93(13)	N(3)–Cu(1)–N(13)	95.26(13)
N(11)–Cu(1)–N(13)	94.57(12)	N(11)–N(12)–N(13)′	177.0(3)
Cu(1)–N(11)–N(2)	122.5(2)	Cu(1)–N(13)–N(12)′	139.4(3)

Table 4 Selected bond lengths (Å) and angles (°) for [Cu$_2$($\mu_{1,1}$-N$_3$)$_2$(Medien)$_2$](ClO$_4$)$_2$ (**3**)

Cu–Cu′	3.343(2)	Cu–N(1)	2.012(3)
Cu–N(2)	2.159(3)	Cu–N(3)	2.027(3)
Cu–N(4)	2.098(3)	Cu–N(4)′	2.513(4)
N(4)–N(5)	1.371(5)	N(5)–N(6)	1.300(5)
N(1)–Cu–N(2)	85.06(15)	N(1)–Cu–N(3)	155.73(15)
N(1)–Cu–N(4)	94.74(15)	N(1)–Cu–N(4)′	100.95(14)
N(2)–Cu–N(3)	86.63(15)	N(2)–Cu–N(4)	177.76(13)
N(2)–Cu–N(4)′	94.73(13)	N(3)–Cu–N(4)	92.68(15)
N(3)–Cu–N(4)′	102.44(16)	N(4)–Cu–N(4)′	87.50(13)
N(4)–N(5)–N(6)	177.9(4)	Cu–N(4)–Cu′	92.50(13)

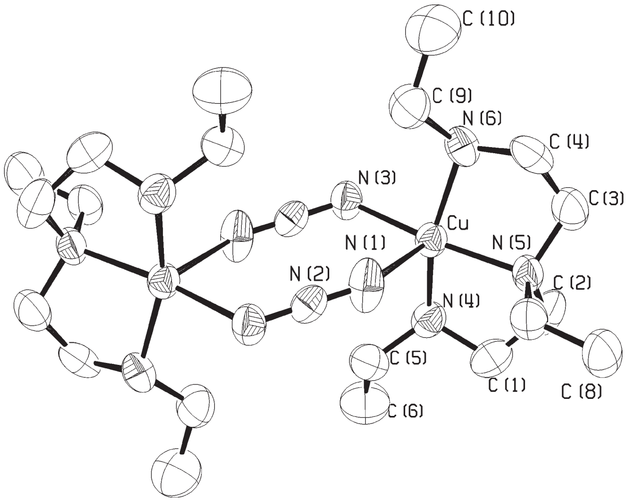

Fig. 1 ORTEP drawing (40% probability) with atom labelling scheme of $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2](ClO_4)_2$ (**1**).

square planar pyramid and a trigonal bipyramid. There are two long Cu–N bonds, one to the central amine N(2) and one to one bridging azide ligand N(4) at 2.159(3) and 2.098(3) Å, respectively. There are two short Cu–N distances, to the end N(1) and N(3) amine atoms at 2.012(3) and 2.027(3) Å, respectively. There is also a very long bond [2.513(4) Å] between Cu and the other bridging azide N(4)′ atom. The Cu–N(4)–Cu′ angle is 92.50(13)°. The central Cu_2N_2 ring is coplanar and has an intradimer Cu–Cu distance of 3.343(1) Å.

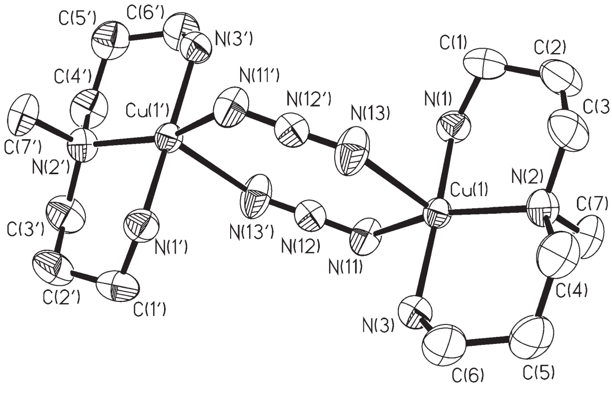

Fig. 2 ORTEP drawing (40% probability) with atom labelling scheme of $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2](ClO_4)_2$ (**2**).

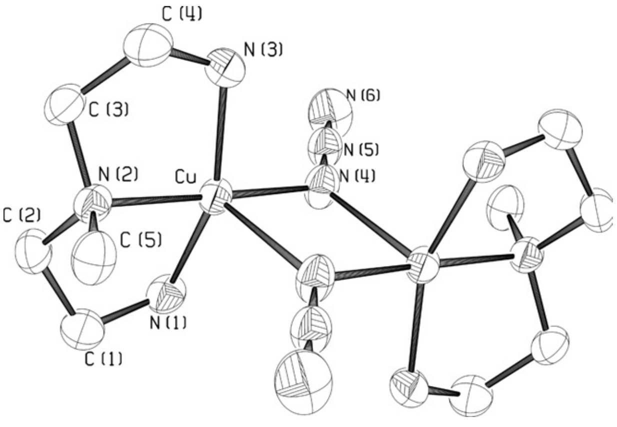

Fig. 3 ORTEP drawing (40% probability) with atom labelling scheme of $[Cu_2(\mu_{1,1}\text{-}N_3)_2(Medien)_2](ClO_4)_2$ (**3**).

Magnetic results

For **1** the $\chi_M T$ value at 230 K (0.822 $cm^3\ mol^{-1}$ K) increases to a maximum (0.981 $cm^3\ mol^{-1}$ K) as the temperature decreases to 4 K, then it decreases to 0.948 $cm^3\ mol^{-1}$ K at 2 K (Fig. 4). For **1**, χ_M increases continuously as the temperature decreases. The magnetic behaviour of **1** indicates ferromagnetic coupling. For **2** the $\chi_M T$ value at room temperature (0.669 $cm^3\ mol^{-1}$ K) decreases as the temperature decreases to a value of 1.65×10^{-3} $cm^3\ mol^{-1}$ K at 2 K, indicating an antiferromagnetic coupling. The χ_M *versus* T plot (Fig. 5) provides more information about the magnetic behaviour of **2**: the χ_M value of 2.23×10^{-3} $cm^3\ mol^{-1}$ at room temperature increases as the temperature decreases, arriving at a maximum of 4.38×10^{-3} $cm^3\ mol^{-1}$ at 97 K; χ_M then decreases practically to zero at 19 K before increasing to a value of 8×10^{-4} $cm^3\ mol^{-1}$ at 2 K. This behaviour clearly indicates a moderately strong antiferromagnetic coupling and the presence of a small amount of paramagnetic impurities. For **3** the $\chi_M T$ value is 0.818 $cm^3\ mol^{-1}$ K at 300 K; it decreases slowly to 0.730 $cm^3\ mol^{-1}$ K as the temperature goes down to 75 K. Below this temperature $\chi_M T$ decreases continuously to a minimum of 0.015 $cm^3\ mol^{-1}$ K at 4 K, indicating a moderate antiferromagnetic coupling. As in the previous compound, there is a maximum in the χ_M *versus* T plot at 14 K (Fig. 6). These measurements newly reveal, in the case of **1** and **2**, the non correlation between magnetic coupling and coordination mode for the asymmetrical doubly-bridged azido copper(II) complexes.

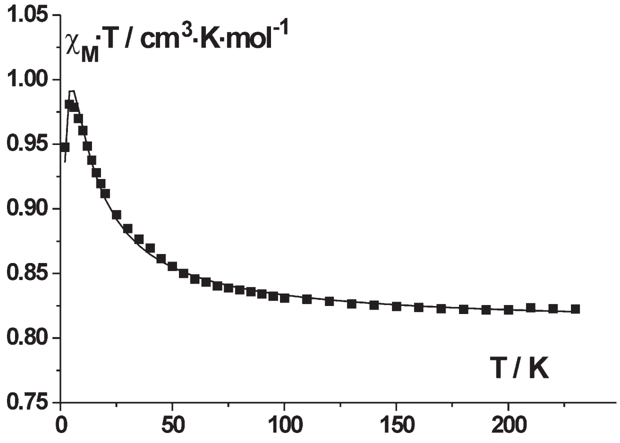

Fig. 4 $\chi_M T$ *vs.* T plot for $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2](ClO_4)_2$ (**1**). Solid lines show the best fit indicated in the text.

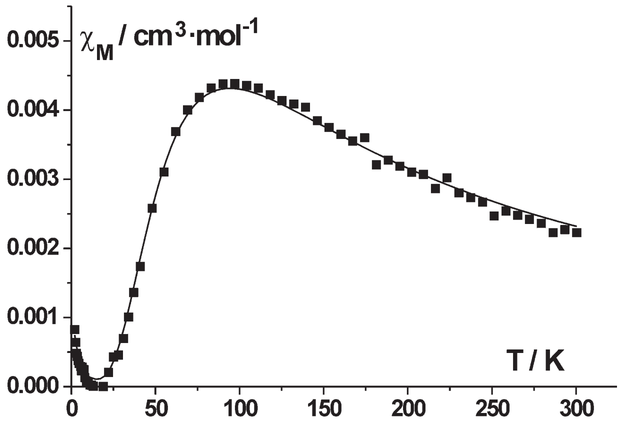

Fig. 5 χ_M *vs.* T plot for $[\mathrm{Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2}](\mathrm{ClO_4})_2$ (**2**). Solid lines show the best fit indicated in the text.

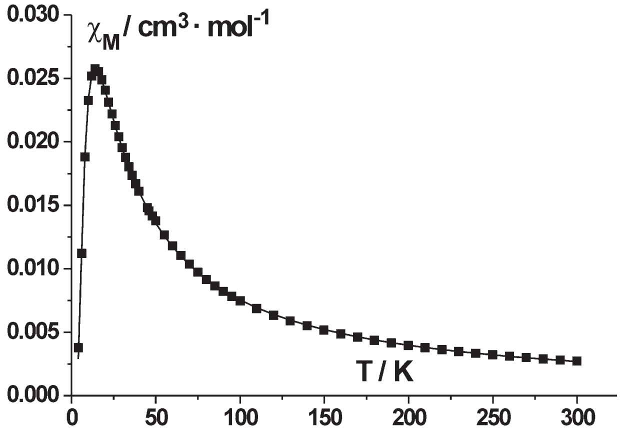

Fig. 6 χ_M *vs.* T plot for $[\mathrm{Cu_2(\mu_{1,1}\text{-}N_3)_2(Medien)_2}](\mathrm{ClO_4})_2$ (**3**). Solid lines show the best fit indicated in the text.

The susceptibility data were fitted to the Bleaney–Bowers[28] expression for the magnetic susceptibility of isotropically coupled $S_1 = S_2 = \frac{1}{2}$ dinuclear compounds, derived from the Hamiltonian $H = -JS_1S_2$. For **1** and **3** the Bleaney–Bowers equation was corrected to take into account the possible additional interactions:[29] zJ' is a parameter representing the intercluster magnetic interactions. For **2**, taking into account the shape of the χ_M *vs.* T plot, the term ρ including the paramagnetic impurities was added to the Bleaney–Bowers expression: ρ is defined as the molar fraction of non-coupled species. r is the agreement factor defined as $\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2$. The results of the best fits, shown as solid lines in Figs. 4, 5 and 6, were $J = 9(2)$ cm^{-1}, $g = 2.078(11)$, $zJ' = -0.32(11)$ cm^{-1} with $r = 2 \times 10^{-5}$ for **1**; $J = -105.2(1)$ cm^{-1}, $g = 2.07(1)$, $\rho = 1.84 \times 10^{-3}$ with $r = 3 \times 10^{-5}$ for **2** and $J = -16.8(4)$ cm^{-1}, $g = 2.07(2)$, $zJ' = -6.0(1)$ cm^{-1} with $r = 1 \times 10^{-4}$ for **3**. The J value of -105 cm^{-1} found in compound **2** is the highest absolute value of J ever reported for asymmetrical doubly-bridged end-to-end azido copper(II) complexes.

To attempt a magnetostructural correlation in the pentacoordinate copper(II) compounds with asymmetric double $\mu_{1,3}$-azido bridges, an important structural parameter is the coordination polyhedron around the copper(II) atom.[14] In general, this can be described as intermediate between a square pyramid (sp) and a trigonal bipyramid (tb). To evaluate the distortion from an ideal square pyramid to a trigonal bipyramid, the τ parameter ($\tau = 0$, square pyramid; $\tau = 1$, trigonal bipyramid) is normally used.[30]

If we define roughly the x and y axes as the equatorial bonds in a pentacoordinate copper(II) compound with asymmetrical double $\mu_{1,3}$-azido bridges, the ideal sp geometry will not be favourable for the transmission of the magnetic coupling because the $d_{x^2-y^2}$ magnetic orbitals, where the unpaired electrons are placed, are not admixed with the d_{z^2} orbitals. Moreover, the ideal tb co-ordination geometry implies that the magnetic orbitals are essentially d_{z^2} orbitals, which permits the existence of a good superexchange pathway. The greater the distortion to a tb geometry, the greater the superexchange interaction should be. In a previous paper,[14] we have used this argumentation to correlate the τ values with the J values of the pentacoordinate copper(II) compounds with asymmetrical double $\mu_{1,3}$-azido bridges known to date. But in the interval, new experimental data for this kind of compound have been added,[16,17] and furthermore we present two more in this paper. In Table 5 the J coupling constants are summarized for the asymmetrical doubly-bridged $\mu_{1,3}$-azido pentacoordinate copper(II) compounds together with the τ parameter: actually, τ alone cannot explain the $|J|$ value. Xie *et al.*[16] have observed this fact and have attempted to predict the $|J|$ value by adding a new structural parameter: the Cu–N3–Cu torsion angle (Δ), which may minimize the antiferromagnetic interaction. Thus, in Table 5 are also summarized the Δ and the R (axial azido nitrogen-to-copper bond length) values. $[\mathrm{Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2}](\mathrm{ClO_4})_2$ (**2**) has the same τ value of 0.23 as $[\mathrm{Cu_2(\mu_{1,3}\text{-}N_3)_2(Me_5dien)_2}](\mathrm{ClO_4})_2$, but the J values are quite different at -150 and -7.5 cm^{-1}, respectively. $[\mathrm{Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2}](\mathrm{ClO_4})_2$ has a Δ value of 11.3° and an R value of 2.31 Å; the same values for $[\mathrm{Cu_2(\mu_{1,3}\text{-}N_3)_2(Me_5dien)_2}](\mathrm{ClO_4})_2$ are 15.7° and 2.33 Å, respectively. Small R and Δ values should enhance the antiferromagnetic coupling. On the other hand, $[\mathrm{Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2}](\mathrm{ClO_4})_2$ (**1**) is ferromagnetically coupled, with a J value of 9 cm^{-1}. The τ value for **1** is 0.20, similar to the τ values of 0.23 found in the aforementioned antiferromagnetically coupled compounds. But **1** has a Δ value of 35.8° and high Δ values seem to enhance the ferromagnetic coupling. For comparative purposes, as it can be seen in Table 5, the ferromagnetically coupled compound $[\mathrm{Cu_2(\mu\text{-}N_3)_2(bben)_2(N_3)_2}]_n$ has τ and Δ values of 0.18 and 47.5°, respectively, and a higher J value of 16.8 cm^{-1}. These experimental facts seem to corroborate that τ is only one of the parameters governing the magnetic coupling in asymmetrical doubly-bridged $\mu_{1,3}$-azido pentacoordinate copper(II) compounds: the Δ parameter seems

Table 5 Selected magnetostructural data for asymmetrical, doubly-bridged, pentacoordinate bis($\mu_{1,3}$)-azido copper(II) complexes

Compound[a]	R^b/Å	τ	Δ/°	J/cm^{-1}	Reference
$[\mathrm{Cu_2(\mu\text{-}N_3)_2(Medpt)_2}](\mathrm{ClO_4})_2$	2.31	0.23	11.3	−105	This work
$[\mathrm{Cu_2(\mu\text{-}N_3)_2(Me_5dien)_2}](\mathrm{ClO_4})_2$	2.33	0.23	15.7	−7.5	14
$[\mathrm{Cu_2(\mu\text{-}N_3)_2(EtMe_4dien)_2}](\mathrm{ClO_4})_2$	2.28	0.28	30.4	−3.6	14
$[\mathrm{Cu_2(\mu\text{-}N_3)_2(Et_3dien)_2}](\mathrm{ClO_4})_2$	2.38	0.20	35.8	9	This work
$[\mathrm{Cu_2(\mu\text{-}N_3)_2(bben)_2(N_3)_2}]_n$	2.37	0.18	47.5	16.8	16

[a] Medpt = methyldipropylenetriamine; Me$_5$dien = 1,1,4,7,7-pentamethyldiethylenetriamine; EtMe$_4$dien = 4-ethyl-1,1,7,7-tetramethyldiethylenetriamine; Et$_3$dien = triethyldiethylenetriamine; bben = 1,2-bis(benzylamino)ethane. [b] Axial azido nitrogen-to-copper bond length.

Table 6 Selected magnetostructural data for asymmetrical, doubly-bridged, pentacoordinate bis($\mu_{1,1}$)-azido copper(II) complexes

Compound[a]	Cu–N–Cu/°	Cu–Cu/Å	R/Å	J/cm^{-1}	Reference
$[Cu_2(\mu\text{-}N_3)_2(dpt)_2](ClO_4)_2$	101.0	3.416	2.398	weak AF	17
$[Cu(\mu\text{-}N_3)_2(phen)]_n$	99.19	3.396	2.449	12.76	18
$[Cu_2(\mu\text{-}N_3)_2(L1)_2](ClO_4)_2$	96.7	3.391	2.536	weak F	19
$[Cu_2(\mu\text{-}N_3)_2(terpy)_2](PF_6)_2$	96.3	3.313	2.469	weak AF	20
$[Cu_2(\mu\text{-}N_3)_2(terpy)_2(H_2O)](PF_6)_2$	95.7	3.595	2.861	−2.9	20
$[Cu(\mu\text{-}N_3)_2(phen)](\mu\text{-}ta)_n$	94.98	2.737	2.461	12.36	21
$[Cu_2(\mu\text{-}N_3)_2(L2)_2]$	86.9	3.166	2.551	24	22
$[Cu_2(\mu\text{-}N_3)_2(Medien)_2](ClO_4)_2$	92.5	3.343	2.513	−16.8	This work

[a] dpt = dipropylenetriamine; phen = 1,10-phenanthroline; L1 = 1-(imidazol-4-yl)-2-[2-pyridylmethylene)amino]ethane; terpy = 2,2′:6′,2″-terpyridine; ta = terephthalato dianion; L2 = 7-amino-4-methyl-5-aza-3-hepten-2-onato(−1); Medien = methyldiethylenetriamine.

to have a major influence on the magnitude and sign of the J value.[16]

On the other hand, the compound $[Cu_2(\mu_{1,1}\text{-}N_3)_2(Medien)_2](ClO_4)_2$ (**3**) joins the short list in the family of dinuclear asymmetric doubly-bridged end-on azido compounds. It is known that symmetric dinuclear $Cu(\mu_{1,1}\text{-}N_3)_2Cu$ compounds are always ferromagnetically coupled[2,4,11] and the same kind of coupling can be expected for the asymmetric ones. But some dinuclear asymmetric doubly-bridged end-on azido compounds show antiferromagnetic coupling,[17,20] as it can be seen in Table 6. The new compound **3** is also antiferromagnetically coupled with a J value of -16.8 cm^{-1}, the highest reported $|J|$ for this family of compounds. From the structural data, it is difficult to justify the magnetic coupling. The τ value is 0.367, which indicates some type of d_{z^2} admixture in the magnetic orbitals, but the Cu–N(azido) distances are a short one of 2.098 Å and a long one of 2.513 Å.

Conclusion

Two asymmetric double $\mu_{1,3}$ (end-to-end) azide-bridged copper(II) compounds, $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Et_3dien)_2](ClO_4)_2$ (**1**) and $[Cu_2(\mu_{1,3}\text{-}N_3)_2(Medpt)_2](ClO_4)_2$ (**2**), have been described. **1** shows unusual ferromagnetic interactions through the end-to-end azido bridges while **2** shows an antiferromagnetic interaction through the end-to-end azido bridges with the highest reported value of $|J|$. The magnetic data of **1** and **2** have been correlated with the Addison parameter, τ, and mainly with the Cu–N_3–Cu torsion angle, Δ. In this paper we have also described the asymmetric double $\mu_{1,1}$ (end-on) azide-bridged copper(II) compound, $[Cu_2(\mu_{1,1}\text{-}N_3)_2(Medien)_2](ClO_4)_2$ (**3**). **3** shows an unusual antiferromagnetic interaction through the end-on azido bridges.

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