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# Crystal structures and magnetic behaviour of three new azido-bridged dinuclear cobalt(II) and copper(II) complexes

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Three dinuclear cobalt(II) and copper(II) complexes with double end-on (EO) azido bridges, $[Co_2(DMP)_2(N_3)_4]$ (**1**), $[Cu_2(DMP)_2(N_3)_4]$ (**2**) and $[Cu_2(PAP)_2(N_3)_4]$ (**3**) (DMP = 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine; PAP = 1-phenyl-2-(2-pyridyl)-1-azapropylene) have been synthesized and characterized by single-crystal X-ray diffraction and magnetic analyses. The EPR spectra of powder samples for the two copper(II) complexes have also been examined at room temperature and 77 K, respectively. In the isomorphous complexes **1** and **2**, the metal ions are penta-coordinated with distorted trigonal bipyramidal geometries, and the EO azido bridges assume an equatorial–axial disposition between metal ions. In contrast, the copper(II) ion in complex **3** adopts a distorted square pyramidal geometry, and the EO azido bridges assume a basal–apical disposition between metal ions. According to magnetic studies, the double end-on azido bridges mediate ferromagnetic coupling with $J = 18.1$ cm$^{-1}$ in **1**, antiferromagnetic coupling with $J = -27.6$ cm$^{-1}$ in **2**, and ferromagnetic coupling with $J = 35.0$ cm$^{-1}$ in **3**.

## Introduction

Investigation into the structural and magnetic properties of polynuclear transition metal complexes is a fascinating subject in the fields of coordination chemistry and molecular magnetism. Due to their broad range of structural and magnetic properties, azido-bridged dinuclear transition metal systems have received considerable attention and provided a good test for theoretical analysis of the exchange coupling.[1,2] The azido anion is a versatile ligand which can link transition metal ions in different coordination modes. It has been widely stated that the exchange is, with some exceptions,[3,4] generally ferromagnetic in nature for the end-on (μ-1,1 or EO) mode, and antiferromagnetic for the end-to-end (μ-1,3 or EE) mode.[5] Although extensive magnetostructural works including DFT calculations[6] have been carried out on azido-bridged dinuclear copper(II),[7] manganese(II),[8] and nickel(II)[9] complexes, the number of dicobalt(II) complexes with such bridges is still limited.[10] Azido-bridged copper(II) complexes are also of great interest for bioinorganic chemists to explore the structure and role of active sites in copper proteins, such as metazido hemocyanins and tyrosinases.[7j,7k] The exchange between Cu(II) ions is strongly dependent upon the coordination geometries of the copper ions and the disposition of the azido bridges. It is noteworthy that most of the double EO azido-bridged dicopper(II) complexes reported so far have shown square pyramidal Cu(II) coordination geometries, and that EO azido-bridged Cu(II) complexes with the trigonal bipyramidal geometry are still unusual.[4d] For complexes in which the EO azido bridge assumes a basal–basal disposition between square pyramidal Cu(II) ions, it has been experimentally and theoretically demonstrated that the exchange is ferromagnetic for lower Cu–N–Cu angles (<108°) and antiferromagnetic for higher angles. The angular dependence seems to be invalid for complexes in which the EO azido bridge assumes a basal–apical disposition.[4d,11,12,13e,13h]

As part of our investigation on metal azides,[13] we report here the synthesis, structure, and magnetic properties of three new dinuclear complexes with double EO azido bridges: $[Co_2(DMP)_2(N_3)_4]$ (**1**), $[Cu_2(DMP)_2(N_3)_4]$ (**2**) and $[Cu_2(PAP)_2(N_3)_4]$ (**3**), where DMP = 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine and PAP = 1-phenyl-2-(2-pyridyl)-1-azapropylene. For the ligand DMP, two mononuclear copper(II) compounds, $[Cu(DMP)_2](ClO_4)_2$ and $[Cu(DMP)_2(ONO)]ClO_4$, have been structurally characterized previously.[14a,b] In the isomorphous complexes **1** and **2**, the metal ions assume a trigonal bipyramidal geometry and are ferromagnetically (**1**) or antiferromagnetically (**2**) coupled, while complex **3** contains square pyramidal Cu(II) ions that are ferromagnetically coupled.

## Experimental

### Materials and physical measurements

All the starting chemicals were of A. R. grade and used as received. The ligands DMP and PAP were prepared according to the literature process.[14c,d] Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan microscope. Magnetic measurements of compound **1** were carried out on a Quantum Design SQUID MPMS XL-7 magnetometer, and those of compounds **2** and **3** on an Oxford MagLab 2000 magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[15] X-band EPR spectra were recorded on a Bruke ER-200D spectrometer.

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**Table 1** Summary of crystallographic data for the three complexes

| | 1 | 2 | 3 |
|---|---|---|---|
| Formula | $C_{22}H_{26}Co_2N_{18}$ | $C_{22}H_{26}Cu_2N_{18}$ | $C_{26}H_{24}Cu_2N_{16}$ |
| Formula weight | 660.46 | 669.68 | 687.71 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $C2/c$ | $C2/c$ | $P2_1/n$ |
| $a$/Å | 24.2866(4) | 24.3949(3) | 12.0150(4) |
| $b$/Å | 8.1348(2) | 8.0468(1) | 6.3940(2) |
| $c$/Å | 18.8753(4) | 18.7195(3) | 19.1148(8) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 128.8435(8) | 128.6544(7) | 102.01(3) |
| $\gamma$/° | 90 | 90 | 90 |
| $U$/Å$^3$ | 2904.47(11) | 2869.64(7) | 1436.35(9) |
| $Z$ | 4 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.510 | 1.550 | 1.590 |
| μ(Mo Kα)/mm$^{-1}$ | 1.190 | 1.531 | 1.530 |
| $T$/K | 293(2) | 293(2) | 293(2) |
| $\theta$ range/° | 3.61–27.48 | 3.41–27.49 | 3.41–27.42 |
| Reflections measured | 29 747 | 24 923 | 19 983 |
| Unique reflections/$R_{int}$ | 3337/0.0524 | 3300/0.0672 | 3215/0.1247 |
| Parameters refined | 193 | 193 | 201 |
| $R_1{}^a$ [$I > 2\sigma(I)$] | 0.0303 | 0.0324 | 0.0467 |
| w$R_2{}^b$ (all data) | 0.0802 | 0.0775 | 0.1128 |
| GOF on $F^2$ | 1.016 | 0.974 | 1.048 |
| $\rho_{max}/\rho_{min}$/e Å$^{-3}$ | 0.354/−0.308 | 0.284/−0.337 | 0.548/−0.573 |

$^a$ $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $^b$ w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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### Synthesis

***CAUTION!*** Metal azide complexes and perchlorate are potentially explosive. Only a small amount of material should be prepared and should be handled with caution.

**[$Co_2$(DMP)$_2$($N_3$)$_4$] (1).** An aqueous solution (20 mL) of DMP (0.5 mmol) and cobalt(II) acetate tetrahydrate (0.5 mmol) was stirred for 5 min, then an aqueous solution (10 mL) containing sodium azide (1.0 mmol) was added with continuous stirring. Slow evaporation of the resulting blue solution at room temperature yielded blue crystals of **1** within two days. Yield, 60.5%. Anal. calcd. for $C_{11}H_{13}N_9Co$: C, 40.01; H, 3.97; N, 38.17. Found: C, 40.16; H, 3.98; N, 38.17%. Main IR bands ($\nu$/cm$^{-1}$): 2063 s, 1603 ms, 1551 ms, 1441 ms, 1311 ms, 1288 ms, 1204 m, 1054 m, 1018 m, 775 m.

**[$Cu_2$(DMP)$_2$($N_3$)$_4$] (2).** A mixture of DMP (0.5 mmol) and copper(II) perchlorate hexahydrate (0.5 mmol) in methanol solution (10 mL) was stirred for 15 min, then a methanol solution (10 mL) containing sodium azide (1.0 mmol) was added with continuous stirring. Slow evaporation of the resulting dark green solution at room temperature yielded dark green crystals of **2**, which were collected after two months. Yield, 50.2%. Anal. calcd. for $C_{11}H_{13}N_9Cu$: C, 39.46; H, 3.91; N, 37.65. Found: C, 39.41; H, 4.12; N, 38.18%. Main IR bands ($\nu$/cm$^{-1}$): 2056 s, 2039 s, 1606 ms, 1551 ms, 1438 ms, 1313 ms, 1292 ms, 1204 m, 781 m.

**[$Cu_2$(PAP)$_2$($N_3$)$_4$] (3).** The complex was prepared in the same way as **2**, using PAP instead of DMP. Yield, 31.7%. Anal. calcd. for $C_{13}H_{12}N_8Cu$: C, 45.41; H, 3.52; N, 32.59. Found: C, 45.25; H, 3.54; N, 32.77%. Main IR bands ($\nu$/cm$^{-1}$): 2052 vs, 1649 m, 1594 s, 1441 m, 1333 m, 1306 m, 1284 m, 1016 m, 774 m, 756 m, 702 m.

### Crystal structure analysis

Diffraction intensity data for single crystals of **1**, **2** and **3** were collected at room temperature on a Nonius Kappa CCD area detector equipped with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.710 73 Å). Empirical absorption corrections were applied using the Sortav program.[16] The structures were solved by direct methods and refined by the full-matrix least-squares method on $F^2$ with anisotropic thermal parameters for all non-hydrogen atoms.[17] Hydrogen atoms were placed geometrically and refined isotropically. Pertinent crystallographic data and structure refinement parameters are summarized in Table 1.†

## Results and discussion

### IR spectra

The IR spectra of the three complexes are similar. In the 2000–2100 cm$^{-1}$ region expected for the $\nu_{as}(N_3)$ absorption, the occurrence of two sharp and strong bands at about 2055 and 2039 cm$^{-1}$ indicates the presence of two different azido groups.[12d] The medium band at *ca.* 1333 cm$^{-1}$ is assignable to the azido symmetric $\nu_s(N_3)$ stretching mode. The $\nu$(C=N) absorption characteristic of the Schiff base ligand PAP occurs at *ca.* 1594 cm$^{-1}$ as a medium band.

### Crystal structures

**[$Co_2$(DMP)$_2$($N_3$)$_4$] (1).** The μ-1,1-$N_3$ bridged dinuclear unit and the packing diagram of **1** are shown in Fig. 1, and selected bond length and bond angle values, including those for hydrogen bonds, are given in Table 2. Five nitrogen atoms from a DMP ligand, a terminal azido ion and two bridging azido ions complete the coordination sphere of the Co(II) ion with a distorted trigonal bipyramidal geometry. The pyridyl nitrogen atom (N1) from the DMP ligand and one (N7A) of the bridging azido ions occupy the axial positions, and the pyrazole nitrogen (N2) from the DMP ligand, a nitrogen atom (N4) from the terminal azido ligand and the other bridging azido nitrogen atom (N7) construct the equatorial trigonal plane. The axial Co–N bond lengths (av. 2.176 Å) are significantly longer than the equatorial ones (av. 2.012 Å). The Co atom is essentially placed in the equatorial plane with a

† CCDC reference numbers 250477 (**1**), 250478 (**2**), and 250479 (**3**). See http://www.rsc.org/suppdata/nj/b4/b418239a/ for crystallographic data in CIF or other electronic format.

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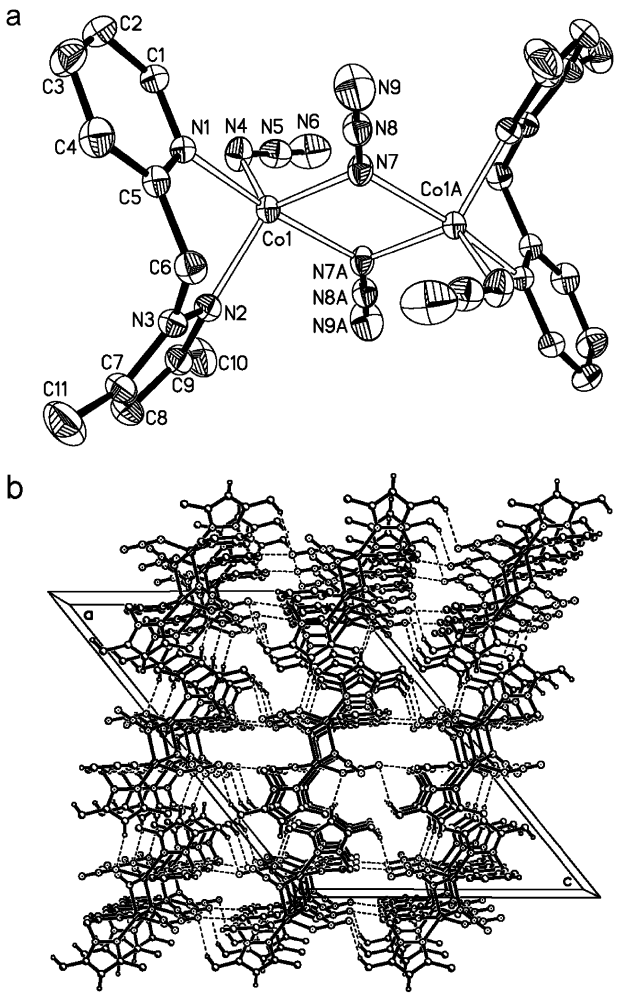


**Fig. 1** Thermal ellipsoid plot (30% probability) with atom-labeling scheme and H-atoms omitted for clarity (a) and the intermolecular hydrogen bond scheme (b) in complex **1**. (Only hydrogen atoms involved in the hydrogen bonds are shown.)

deviation of only 0.0002 Å. The distortion along the axial direction is demonstrated by the N1–Co1–N7A angle of 169.00(5)°. According to Addison *et al.*,[18] the distortion of the square pyramidal geometry towards trigonal bipyramidal can be described by the geometrical parameter $\tau = |\beta - \alpha|/60$, where $\beta$ and $\alpha$ are the bond angles involving the *trans* donor atoms in the basal plane. The $\tau$ value for **1** is 0.77, confirming the trigonal bipyramidal geometry. All azido ions in the structure are quasi-linear with the N–N–N angles being 179.4(2)° and 178.1(3)° for bridging and terminal ones, respectively. They also exhibit relatively asymmetric N–N distances. The bridging angle Co1–N7–Co1A is 102.29(6)°, which falls in the usual 100–107° range found for Cu(II), Ni(II) and Mn(II) complexes.[7m] The Co···Co distance in the double EO azido bridging moiety is 3.2931(4) Å. It is interesting to note that the EO azido nitrogen atom assumes an asymmetric equatorial–axial disposition between the two Co(II) ions; *i.e.*, the same azido bridge resides on the axial position of one cobalt center but in the equatorial plane of the other cobalt center. Although no classical N–H hydrogen bonds are observed, very weak C–H···N hydrogen bonds (C···N distances vary from 3.346 to 3.475 Å, and C–H···N angles from 153.86 to 167.7°, see Table 2) are observed to exist between neighboring dimers. The shortest interdimer Co···Co distance is 6.6946(5) Å between Co1 and Co1E (symmetry code E: $-x$, $1 - y$, $-z$).

**$[Cu_2(DMP)_2(N_3)_4]$ (2).** Complex **2** is isomorphous with **1**. Selected distances and angles are listed in Table 2. The Cu(II) ion adopts a distorted trigonal bipyramidal geometry and is displaced out of the equatorial plane by 0.0203 Å. The distortion geometrical parameter $\tau$ is 0.64. Again, the azido bridge assumes an asymmetric equatorial–axial disposition between the two Cu(II) ions in the dinuclear unit, with the axial Cu–N(azido) distance being significantly longer than the equatorial Cu–N(azido) one. The Cu–N–Cu bridging angle and the Cu···Cu distance are 103.04(9)° and 3.3243(5) Å, respectively. Weak C–H···N hydrogen bonds (C···N distances vary from 3.379 to 3.464 Å, and C–H···N angles from 149.48 to 171.5°, see Table 2) exist between neighboring dimers. The shortest interdimer Cu···Cu distance is 6.927 Å.

**Table 2** Selected bond distances (Å) and angles (°) for complexes **1** and **2**

| | | **1** | **2** |
|---|---|---|---|
| M(1)–N(4) | | 1.9686(17) | 1.9803(19) |
| M(1)–N(7) | | 2.0288(14) | 2.2455(18) |
| M(1)–N(2) | | 2.0415(15) | 2.0369(17) |
| M(1)–N(1) | | 2.1534(15) | 2.0385(16) |
| M(1)–N(7A) | | 2.1977(15) | 1.9960(17) |
| N(7)–N(8) | | 1.203(2) | 1.194(2) |
| N(8)–N(9) | | 1.145(2) | 1.145(3) |
| N(4)–N(5) | | 1.201(3) | 1.187(2) |
| N(5)–N(6) | | 1.153(3) | 1.151(3) |
| N(4)–M(1)–N(7) | | 119.05(7) | 110.99(8) |
| N(4)–M(1)–N(2) | | 118.09(7) | 126.34(8) |
| N(7)–M(1)–N(2) | | 122.86(7) | 122.63(7) |
| N(4)–M(1)–N(1) | | 93.11(7) | 92.57(7) |
| N(7)–M(1)–N(1) | | 91.64(6) | 88.21(6) |
| N(2)–M(1)–N(1) | | 85.37(6) | 87.68(6) |
| N(4)–M(1)–N(7A) | | 94.47(7) | 95.92(8) |
| N(7)–M(1)–N(7A) | | 77.71(6) | 76.95(8) |
| N(2)–M(1)–N(7A) | | 98.03(6) | 97.36(7) |
| N(1)–M(1)–N(7A) | | 169.00(5) | 164.76(7) |
| N(8)–N(7)–M(1) | | 124.50(13) | 124.44(14) |
| N(8)–N(7)–M(1A) | | 132.81(12) | 130.74(15) |
| M(1)–N(7)–M(1A) | | 102.29(6) | 103.05(8) |
| N(9)–N(8)–N(7) | | 179.4(2) | 177.3(2) |
| N(6)–N(5)–N(4) | | 178.1(3) | 178.0(3) |
| *Hydrogen bonds* | | | |
| C3–H···N6B | C3···N6B distance | 3.346 | 3.379 |
| | C3–H···N6B angle | 159.65 | 159.77 |
| C8–H···N4C | C8···N4D distance | 3.405 | 3.419 |
| | C8–H···N4D angle | 167.66 | 171.51 |
| C11–H···N6D | C11···N6E distance | 3.475 | 3.464 |
| | C11–H···N6E angle | 153.86 | 149.48 |

Symmetry codes: A: $-x$, $2 - y$, $-z$; B: $x$, $1 - y$, $0.5 + z$; C: $0.5 - x$, $0.5 + y$, $0.5 - z$; D: $x$, $2 - y$, $0.5 + z$.

**$[Cu_2(PAP)_2(N_3)_4]$ (3).** The molecular structure of complex **3** is depicted in Fig. 2a, with relevant bond lengths and bond angles, including those for hydrogen bonds, given in Table 3. Each Cu(II) ion is penta-coordinated by a PAP Schiff base ligand, a terminal azido ion and two bridging azido ions. Two Cu(II) are linked by double EO azido bridges to form a dimer. Unlike that in **2**, the coordination geometry of Cu(II) in **3** is distorted square pyramidal, indicated by the geometrical parameter $\tau$ of 0.083, with one of the bridging azido nitrogen atoms at the apical position. The Cu(II) ion deviates from the basal plane by 0.106(1) Å. Each EO azido ion bridges in an asymmetric basal–apical mode with the apical Cu–N bond significantly longer than the basal one by about 0.51 Å. The Cu···Cu distance and the Cu–N–Cu bridging angle in the dimer are 3.25 Å and 92°, respectively, which fall in the range for dinuclear Cu(II) compounds with the same bridging mode of azido ions.[11,13e] Along the *b* direction, the $[CuN_4]$ coordination basal planes of the dimer are parallel to each other with an

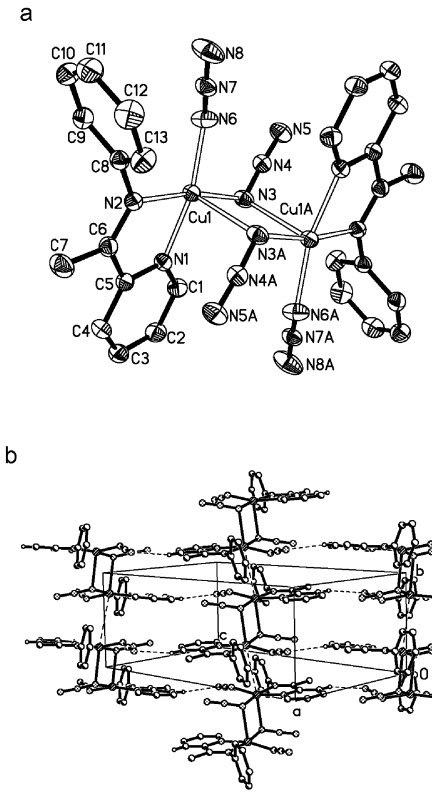


**Fig. 2** Thermal ellipsoid plot (30% probability) with atom-labeling scheme and H-atoms omitted for clarity (a) and the intermolecular hydrogen bond scheme between neighboring chains (b) in **3**.

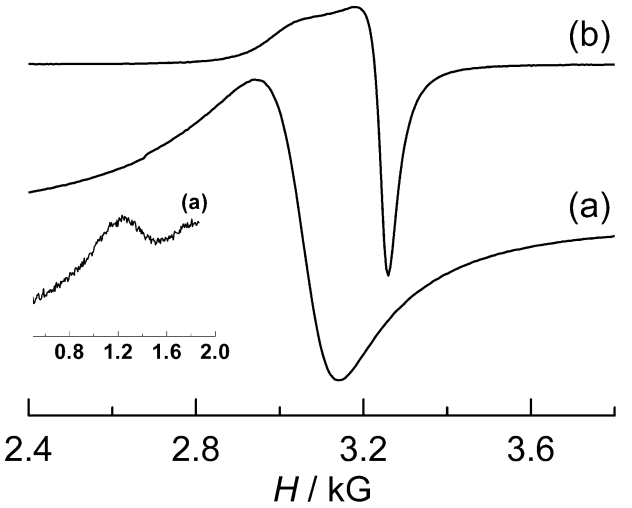


**Fig. 3** X-band EPR spectra of powder samples of **2** (a) and **3** (b) at 77 K with frequency = 9.324 28 GHz.

interplanar distance of 3.54 Å and a Cu···Cu separation of 3.78 Å. These features indicate a weak stacking interaction between the [$CuN_4$] basal planes of the dimers, which results in a chain of dimers along the *b* direction (Fig. 2b). Very weak C–H···N hydrogen bonds exist between the pyridyl groups and azido ions of the neighboring chains with the C···N distance 3.30 Å and C–H···N angle 150.1° (Table 3). The neighboring chains are separated well with the shortest distance being 10.18 Å.

## EPR spectra and magnetic results

Solid X-band EPR spectra were recorded for complexes **2** and **3** at room temperature and 77 K, and the spectra at 77 K are drawn in Fig. 3. Compound **2** exhibits a broad quasi-isotropic signal centered at $g_{iso} = 2.19$ (Fig. 3a), corresponding to the $\Delta M_S = \pm 1$ transition. The very weak maximum detected at about 1232 G is attributable to the "half-field" $\Delta M_S = \pm 2$ transition, indicating the presence of intradimer magnetic exchange between Cu(II).[19] The room temperature spectrum of **2** is very similar to that at 77 K, except that the "half-field" signal is slightly stronger. This is consistent with the antiferromagnetic nature of the intradimer exchange. For compound **3**, both EPR spectra at room temperature and at 77 K show an axial symmetry (Fig. 3b) with $g_{\|} = 2.21$ and $g_{\perp} = 2.06$, in accord with the square pyramidal geometry around copper(II). The "half-field" signal is not observed for **3**, maybe due to the interactions between dimers.

The magnetic susceptibility of complex **1** was measured in the 2–300 K temperature range and is shown as $\chi_M T$ and $\chi_M$ *versus* *T* plots in Fig. 4. The measured $\chi_M T$ value at 300 K is 6.08 emu mol$^{-1}$ K per dimer, higher than the spin-only value of 3.76 emu mol$^{-1}$ K for two uncoupled $S = 3/2$ spins. With decreasing the temperature, the $\chi_M T$ value increases smoothly to a maximum value of 7.71 emu mol$^{-1}$ K at *ca.* 30 K, then decreases sharply to 1.87 emu mol$^{-1}$ K at 2 K. The increase of $\chi_M T$ above 30 K indicates the presence of intramolecular ferromagnetic interactions, and the low-temperature drop may be due to secondary effects such as intermolecular antiferromagnetic interactions and/or zero-field splitting effects. On account of the distorted trigonal bipyramidal geometry of the Co(II) center and the $^4A_2'$ ground state with no angular momentum, the Heisenberg spin Hamiltonian $H = -JS_1 \cdot S_2$ should be applicable, where *J* is the intradimer interaction

**Table 3** Selected bond distances (Å) and angles (°) for complex **3**

| | | | | |
|---|---|---|---|---|
| Cu(1)–N(6) | | 1.929(3) | Cu(1)–N(1) | 2.014(3) |
| Cu(1)–N(3) | | 1.993(3) | Cu(1)–N(2) | 2.019(3) |
| Cu(1)–N(3A) | | 2.500(3) | N(6)–N(7) | 1.184(4) |
| N(3)–N(4) | | 1.212(4) | N(7)–N(8) | 1.144(5) |
| N(4)–N(5) | | 1.150(4) | | |
| N(6)–Cu(1)–N(3) | | 91.1(1) | N(6)–Cu(1)–N(3A) | 103.6(1) |
| N(6)–Cu(1)–N(1) | | 164.6(1) | N(3)–Cu(1)–N(3A) | 88.0(1) |
| N(3)–Cu(1)–N(1) | | 91.1(1) | N(1)–Cu(1)–N(3A) | 91.63(9) |
| N(6)–Cu(1)–N(2) | | 99.2(1) | N(2)–Cu(1)–N(3A) | 88.11(9) |
| N(3)–Cu(1)–N(2) | | 169.6(1) | N(5)–N(4)–N(3) | 176.2(3) |
| N(1)–Cu(1)–N(2) | | 79.4(1) | N(8)–N(7)–N(6) | 175.5(4) |
| Cu(1)–N(3)–Cu(1A) | | 92.0(1) | | |
| *Hydrogen bonds* | | | | |
| C4–H···N8B | C4···N8B distance | 3.296 | | |
| | C4–H4···N8B angle | 150.1 | | |

Symmetry codes: A: $-x$, $1 - y$, $-z$; B: $0.5 + x$, $0.5 - y$, $0.5 + z$.

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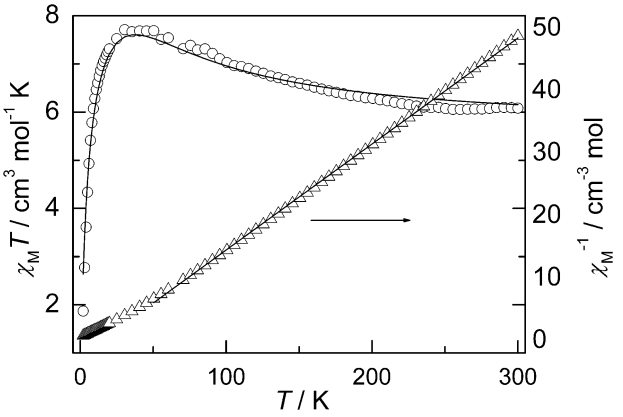


**Fig. 4** $\chi_M^{-1}$ and $\chi_M T$ *versus* $T$ plots for complex **1**. The solid lines represent the best fit to the experimental data.

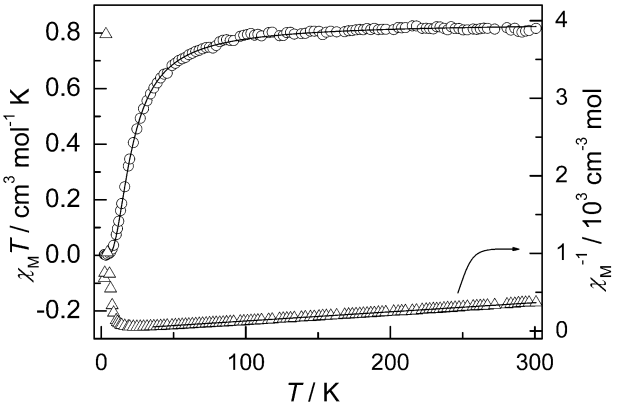


**Fig. 5** $\chi_M^{-1}$ and $\chi_M T$ *versus* $T$ plots for complex **2**. The solid lines represent the best fit to the experimental data.

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parameter between Co(II) ions. Thus the magnetic data were fitted by eqn. (1):[20]

$$\chi_{dim} = (2N\beta^2g^2/kT)[(e^{5x} + 5e^{3x} + 14)/(e^{6x} + 3e^{5x} + 5e^{3x} + 7)] \quad (1)$$

where $x = -J/kT$. Based on the Heisenberg spin Hamiltonian $H = -zJ'\langle S_z\rangle \cdot S_z$, the interdimer interaction ($zJ'$) was accounted for by the molecular-field approximation:[15]

$$\chi_M = \chi_{dim}/[1 - (zJ'/Ng^2\beta^2)\chi_{dim}] \quad (2)$$

The least squares fit of the experimental data above 2 K to the above expressions led to $g = 2.45$, $J = 18.1$ cm$^{-1}$ and $zJ' = -0.84$ cm$^{-1}$. Although the $^4A_2'$ ground state for Co(II) with trigonal bipyramidal geometry has no orbital angular momentum, the fitted $g$ value deviated significantly from 2.00. This may be explained by the admixture of the $^4E''$ excited state, which brings a second-order orbital momentum into the ground state.[10e] Dicobalt(II) complexes with trigonal bipyramidal geometry and EO azido bridges are very rare, and to the best of our knowledge only two complexes have been characterized by both single-crystal X-ray diffraction and magnetic analyses. One contains 2,9-dimethyl-1,10-phenanthroline as the terminal ligand,[10b] for which the fitted $g$ and $J$ values ($g = 2.56$, $J = 14.3$ cm$^{-1}$) are in good agreement with the present complex. The other complex contains an imino nitroxide radical as the terminal ligand,[10a] and the magnetic interaction *via* the double EO bridges has also been proposed to be ferromagnetic, although the fitted interaction parameter (17.7 cm$^{-1}$) refers to the coupling between the Co(II)-radical subunits. Ferromagnetic interactions have also been found in double EO azido-bridged dicobalt(II) complexes with octahedral or tetrahedral coordination geometry (Table 4). This is consistent with Mn(II) and Ni(II) complexes in which the EO azido bridge also propagates ferromagnetic interactions.

The temperature dependence of the magnetic susceptibility of complex **2** is shown as a $\chi_M T$ *versus* $T$ plot in Fig. 5. The $\chi_M T$ value per dimer at 300 K is 0.82 emu mol$^{-1}$ K. Upon cooling, the $\chi_M T$ product decreases monotonically and tends to zero at low temperature, while the $\chi_M$ value increases to a rounded maximum of about 0.018 emu mol$^{-1}$ at *ca.* 23 K and then decreases rapidly on further cooling. These features indicate an antiferromagnetic interaction in this compound. The well-known Bleaney–Bowers equation derived from the Hamiltonian $H = -JS_1 \cdot S_2$ [eqn. (3)][21] modified by the molecular-field approximation [eqn. (2)] was fitted to the experimental data:

$$\chi_{dim} = (2N\beta^2g^2/kT)[3 + \exp(-J/kT)]^{-1} \quad (3)$$

The least squares fit of the above expressions to the experimental data above 2 K led to $g = 2.12$, $J = -27.6$ cm$^{-1}$ and $zJ' = 5.82$ cm$^{-1}$. The negative $J$ value confirms the antiferromagnetic nature.

The magnetic susceptibility of complex **3** was measured in the range 2–300 K and the $\chi_M T$ and $\chi_M^{-1}$ *versus* $T$ plots are shown in Fig. 6. The $\chi_M T$ value per dimer at 300 K is 0.89 emu mol$^{-1}$ K. Upon cooling to 2 K, the $\chi_M$ value increases monotonically but the $\chi_M T$ value increases to a maximum at 16 K, suggesting overall ferromagnetic interactions. The low temperature drop of $\chi_M T$ may be due to the secondary antiferromagnetic interactions and/or zero-field splitting effects.

According to the structural data, the dicopper molecules in **3** are not well separated, and neighboring dimers interact with each other *via* the [CuN$_4$] basal plane stacking interactions to give rise to the supramolecular chains, with short interdimer Cu···Cu distances (*ca.* 3.78 Å). Therefore, magnetically, the complex may be described as a chain in which two different interactions alternate: the intradimer interaction through the double EO azido bridges and the interdimer one *via* the [CuN$_4$] basal plane interaction. To simulate the experimental data, we applied a "chain of dimers" model:[22]

$$\chi_{chain} = (N\beta^2g^2/3kT)S_d(S_d + 1)(1 + u)/(1 - u) \quad (4)$$

where $u = \coth(J_cS_d(S_d + 1)/kT) - kT/J_cS_d(S_d + 1)$, $S_d(S_d + 1) = 6/[3 + \exp(-J_d/kT)]$, $S_d$ is the effective spin of the dimer,

**Table 4** Selected magneto-structural data for double end-on azido-bridged dinuclear cobalt(II) complounds

| Compound[a] | Co–Co/Å | Co–N–Co/° | $J$/cm$^{-1}$ | $g$ | Geometry | Ref. |
|---|---|---|---|---|---|---|
| $[Co_2(immepy)_2(N_3)_4]\cdot 2EtOH$ | 3.344 | 103.4 | 17.7 | 2.08 | TBP | 10*a* |
| $[Co_2(DMphen)_2(N_3)_4]$ | 3.325 | 104.96 | 14.3 | 2.556 | TBP | 10*b* |
| $[Co_2(N_3)_2L^1]\cdot(ClO_4)_2\cdot 4H_2O$ | | | 9 | 2.40 | | 10*c* |
| $[Co_2(N_3)_2L^2]\cdot(ClO_4)_2\cdot 2MeCN$ | 3.277 | 104.8 | 12 | 2.50 | [b] | 10*c* |
| $[Co_2(DMP)_2(N_3)_4]$, **1** | 3.293 | 102.29 | 18.1 | 2.45 | TBP | This work |

[a] immepy = 4,4,5,5-tetramethyl-2-(6′-methyl-2′-pyridyl)imidazoline-1-oxyl; DMphen = 2,9-dimethyl-1,10-phenanthroline; $L^1$ and $L^2$ were described as macrocyclic ligands in ref. 7*d* and 7*l*; DMP = 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine. [b] The geometry about the cobalt atom can be described as a distorted octahedron.

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**Table 5** Selected magneto-structural data for double end-on azido-bridged dinuclear copper(II) compounds

| Dimer[a] | Cu–Cu/Å | Cu–N–Cu/° | $J$/cm$^{-1}$ | $g$ | $\tau$ | Ref. |
|---|---|---|---|---|---|---|
| $[Cu_2(tbz)_2(N_3)_4](CH_3OH)_2$ | 3.242 | 104.66 | 23 | 2.14 | 0.008 | 7*f* |
| $[Cu_2(N_3)_2(L)_2]$ | 3.166 | 86.9 | 24 | 2.02 | 0.177 | 12*b* |
| $[Cu_2(N_3)_4(phen)_2]_n$ | 3.396 | 99.19 | 12.76 | 2.11 | 0.068 | 7*b* |
| $[Cu_2(N_3)_2(phen)_2](\mu$-ta) | 2.737 | 94.89 | 12.36 | 2.05 | 0.088 | 7*g* |
| $[Cu_2(dpt)_2(N_3)_2](ClO_4)_2$ | 3.416 | 101.0 | weak AF | 2.012 | 0.282 | 12*a* |
| | 3.314 | 100.7 | | | 0.492 | |
| $[Cu_2(N_3)_2(L')_2](ClO_4)_2$ | 3.391 | 96.7 | weak F | 2.11 | 0.015 | 7*d* |
| $[Cu_2(N_3)_2(terpy)_2](PF_6)_2$ | 3.313 | 96.3 | weak AF | 2.12 | 0.145 | 7*i* |
| $[Cu_2(N_3)_2(terpy)_2(H_2O)](PF_6)_2$ | 3.595 | 95.7 | −2.9 | 2.12 | [b] | 7*i* |
| $[Cu_2L^a_2(N_3)_2]$ | 3.181 | 89.1 | −8.5 | 2.10 | 0.177 | 11 |
| $[Cu_2(N_3)_2(Medien)_2](ClO_4)_2$ | 3.343 | 92.5 | −16.8 | 2.07 | 0.367 | 4*d* |
| $[Cu_2(aepi)_2(N_3)_4]$ | 3.348 | 98.84 | −3.06 | 2.09 | 0.15 | 4*g* |
| $[Cu_2(N_3)_4(L_1)_2]$ | 3.318 | 93.60 | 2.9 | 2.11 | 0.26 | 4*f* |
| $[Cu_2(N_3)_4(L_2)_2]$ | 3.193 | 90.50 | −1.8 | 2.11 | 0.02 | 4*f* |
| $[Cu_2(N_3)_4(L_3)_2]$ | 3.161 | 86.82 | −3.1 | 2.12 | 0.17 | 4*f* |
| $[Cu_2(N_3)_4(L^1)_2]$ | 3.106 | 88.3 | −2.63 | 2.11 | 0.13 | 4*e* |
| $[Cu_2(N_3)_4(L^2)_2]$ | 3.232 | 93.0 | −1.79 | 2.13 | 0.23 | 4*e* |
| $[Cu_2(N_3)_4(L^3)_2]$ | 3.273 | 90.8 | −5.37 | 2.14 | 0.21 | 4*e* |
| $[Cu_2(DMP)_2(N_3)_4]$, **2** | 3.32 | 103.05 | −27.6 | 2.12 | 0.64 | This work |
| $[Cu_2(PAP)_2(N_3)_4]$, **3** | 3.251 | 92.01 | 35.0 | 2.13 | 0.083 | This work |

[a] tbz = bis(2-benzimidazolyl)propane; L = 7-amino-4-methyl-5-aza-3-hepten-2-onato(1−); phen = 1,10-phenanthroline; ta = terephthalato dianion; dpt = dipropylenetriamine; L′ = 1-(imidazol-4-yl)-2-([2-pyridyl-methylene]amino)ethane; terpy = 2,2′:6′,2″-terpyridine; $L^a$ = 1-(*N*-salicylideneamino)-2-aminoethane; Medien = methyldiethylenetriamine; aepi = 1-(2-aminoethyl)piperidine; $L_1$ = 8-amino-4-methyl-5-azaoct-3-en-2-one; $L_2$ = *N*-(3-aminopropyl)salicylaldimine; $L_3$ = 7-amino-4-methyl-5-azahept-3-en-2-one; $HL^1$ = *N*-[2-(ethylamino)ethyl]salicylaldimine; $HL^2$ = 7-(ethylamino)-4-methyl-5-azahept-3-en-2-one; HL3 = 7-amino-4-methyl-5-azaoct-3-en-2-one; PAP = 1-phenyl-2-(2-pyridyl)-1-azapropylene. [b] The geometry about the copper atom can be described as essentially a distorted octahedron.

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$J_d$ is the intradimer exchange constant, and $J_c$ is the constant for interdimer coupling.

The best fit of eqn. (4) to the experimental data yielded $g$ = 2.13, $J_d$ = 35.0 cm$^{-1}$ and $J_c$ = −0.44 cm$^{-1}$ (all $J$ values are based on $H = -JS_1 \cdot S_2$). These values indicate alternating ferromagnetic–antiferromagnetic interactions along the supramolecular chain.

A number of double EO azido-bridged dicopper complexes have been structurally and magnetically described. Some selected structural and magnetic data for these complexes are summarized in Table 5. In most of these complexes, the metal ion assumes a penta-coordinated square pyramidal coordination geometry with different degrees of distortion towards trigonal bipyramidal geometry, and the azido bridge adopts a basal–apical asymmetric disposition between metal ions. As can be seen, the coordination geometry of the metal ion in complex **2** shows the largest distortion ($\tau$ = 0.64), and we have described it as a distorted trigonal bipyramid. Although the Cu–N–Cu angles (86–105°) for all these complexes are smaller than 108°, the magnetic interactions between Cu(II) ions vary from antiferromagnetic to ferromagnetic, suggesting that the angular dependence proposed for symmetric azido bridges is not valid for asymmetric bridges.

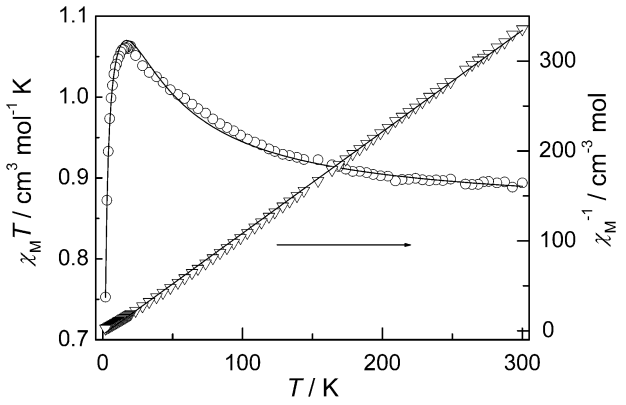


**Fig. 6** $\chi_M^{-1}$ and $\chi_M T$ *versus* $T$ plots for complex **3**. The solid lines represent the best fit to the experimental data.

## Conclusions

In this paper, we have presented the structural and magnetic characterizations of a dinuclear cobalt(II) complex (**1**) and two dinuclear copper(II) complexes (**2** and **3**) with double end-on azido bridges and bidentate ligands. In complexes **1** and **2**, the metal ions assume a distorted trigonal bipyramidal geometry and the azido bridge adopts an equatorial–axial disposition between metal ions. Magnetic investigations suggested that the intradimer magnetic coupling is ferromagnetic for **1**, but antiferromagnetic for **2**. Especially, although many double EO azido-bridged copper(II) compounds have been reported, the $\tau$ value (0.64) of compound **2** is the highest one, which indicates a distorted trigonal bipyramidal geometry and a typical type of $d_z^2$ magnetic orbital for the Cu(II) ion. In **3**, the copper atoms assume square pyramidal geometries and the azido bridges adopt a basal–apical disposition between metal ions. Magnetic properties for **3** indicate the presence of alternate intradimer ferromagnetic and interdimer antiferromagnetic coupling, mediated by the azido bridges and the $[CuN_4]$ basal plane interactions, respectively.

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