## **Electronic Supplementary Information to**

# A Cu-Zn-Cu-Zn heterometallomacrocycle shows significant antiferromagnetic coupling between paramagnetic centres mediated by diamagnetic metal

Elena A. Buvaylo,<sup>a</sup> Vladimir N. Kokozay,<sup>a</sup> Olga Yu. Vassilyeva,<sup>a</sup> Brian W. Skelton,<sup>b</sup> Julia Jezierska,<sup>c</sup> Louis C. Brunel<sup>d</sup> and Andrew Ozarowski<sup>\*d</sup>

<sup>a</sup> Department of Inorganic Chemistry, National Taras Shevchenko University, Volodimirska str. 64, Kyiv 01033, Ukraine<sup>b</sup> Chemistry, School of Biomedical and Chemical Sciences, University of Western Australia, Crawley, Western Australia 6009

<sup>c</sup> Faculty of Chemistry, University of Wroclaw, 14 Joliot-Curie Str., 50-383 Wroclaw, Poland

<sup>d</sup> National High Magnetic Field Laboratory, FSU • 1800 E. Paul Dirac Dr., Tallahassee, FL 32310-3706, USA, Fax: 850-644-1366; Tel: 850-644-5996; E-mail: ozarowsk@magnet.fsu.edu

# Supplementary Material (ESI) for Chemical Communications

# This journal is  $\mathbb O$  The Royal Society of Chemistry 2005



The 30 K spectrum of 1 at 377.24 GHz

Blue: experimental, Red: spin-doublet spectrum simulated with the following parameters:  $g_x = 2.0525 \ g_y = 2.0546 \ g_z = 2.2510$ 

Anisotropic line shape, 50% Gaussian 50% Lorentzian, with the widths x=30 G, y=25 G, z=80 G. Linewidth is defined here for the derivative line as the distance from the zero-point to the peak.

The spectrum can be simulated as coming from an S=1/2 state because the fine structure is lost due to the intermolecular interactions.



The 10 K spectrum of 1 at 92.7675 GHz

Blue: experimental, Red and Green: spin-triplet spectra simulated with the following parameters:

Green:  $g_x = 2.0527 \ g_y = 2.0550 \ g_z = 2.2507$   $D = -108 \ Gauss, E = 6 \ Gauss$ Red:  $g_x = 2.0527 \ g_y = 2.0550 \ g_z = 2.2507$  $D = 108 \ Gauss, E = -6 \ Gauss$ 

To convert *D*, *E* from Gauss to cm<sup>-1</sup> multiply by  $4.6686 \cdot 10^{-5} \cdot 2.0023$ 

For both simulated spectra:

*Z* axis of the zero-field splitting tensor parallel to  $g_x$  $A_x = A_y = 0$ ,  $A_z = 80$  Gauss,  $A_z$  parallel to  $g_z$ To convert  $A_i$  from Gauss to cm<sup>-1</sup> multiply by 4.6686  $\cdot 10^{-5} \cdot g_i$ Isotropic line 40% Gaussian 60% Lorentzian, 20 Gauss width



The 'perpendicular' region of the 10 K spectrum of 1 at 321.600 GHz

Blue: experimental, Red and Green: spin-triplet spectra simulated with the following parameters:

Red:  $g_x = 2.0529 \ g_y = 2.0548 \ g_z = 2.2507$   $D = 108 \ Gauss, E = -6 \ Gauss$ Green:  $g_x = 2.0529 \ g_y = 2.0548 \ g_z = 2.2507$  $D = -108 \ Gauss, E = 6 \ Gauss$ 

To convert *D*, *E* from Gauss to cm<sup>-1</sup> multiply by  $4.6686 \cdot 10^{-5} \cdot 2.0023$ 

For both simulated spectra:

*Z* axis of the zero-field splitting tensor parallel to  $g_x$  $A_x = A_y = 0$ ,  $A_z = 80$  Gauss,  $A_z$  parallel to  $g_z$ To convert A<sub>i</sub> from Gauss to cm<sup>-1</sup> multiply by 4.6686  $\cdot 10^{-5} \cdot g_i$ Isotropic line shape 40% Gaussian 60% Lorentzian, 20 Gauss width



X-Band (9.391 GHz) spectrum of 1 at 10 K.



The 3.0 K spectrum of 1 at 92.767 GHz Blue: experimental, Red: spin-doublet spectrum simulated with the following parameters:  $g_x = 2.0512 g_y = 2.0548 g_z = 2.2480$  $A_x=0, A_y=0, A_z=176$  Gauss Anisotropic line width 50% Gaussian 50% Lorentzian, x=20 G, y=20 G, z=30 G

Magnetic susceptibility per  $\frac{1}{2}$  of the molar mass of 1

Temperature, K	$10^6 \chi$ , cgs emu
4.50	1010
4.30	045
5.00	943
5.50	861
7.00	801
7.00	000
0.00	990
9.00	1211
10.00	2200
12.00	2399
14.00	<u> </u>
10.00	4180
18.00	4930
20.00	<u> </u>
25.00	6392
30.00	6647
35.00	6364
40.00	6347
45.00	60/4
50.00	5/80
55.00	5212
60.00	5212
64.99	4951
70.00	4/11
74.99	4489
/9.99	4285
84.99	4098
89.99	3920
94.99	3763
100.00	3615
109.99	3348
119.99	3117
129.99	2917
139.99	2739
149.99	2580
159.98	2440
169.98	2316
179.98	2205
189.98	2103
199.98	2011
209.98	1928

219.98	1847
229.98	1777
239.98	1712
249.97	1651
259.98	1594
269.99	1541
279.99	1491
289.99	1444
299.99	1401

Note: To convert the molar susceptibility from cgs emu to SI units multiply the molar cgs emu value by  $4\pi \cdot 10^{-6}$ 

#### Contribution of the dipole-dipole and exchange interaction to the Zero-Field splitting

The relations between components of the diagonalized zero-field splitting tensor D and the D and E parameters of the Spin Hamiltonian are

$$D = (2D_{zz} - D_{xx} - D_{yy}) / 2, \qquad E = (D_{xx} - D_{yy}) / 2 \qquad (1)$$

The magnetic dipole-dipole interaction and the anisotropy of the exchange interactions contribute to the *D* tensor components:

$$\boldsymbol{D} = \boldsymbol{D}_{\rm dip} + \boldsymbol{D}_{\rm ex} \tag{2}$$

(Symbols in boldface represent tensors).

The molecule of **1** is centrosymmetric and the formula for the components of the dipolar interaction tensor  $D_{dip}$  given in ref. 11 simplifies to

$$(D_{dip})_{kl} = g_k g_l (\delta_{kl} - 3\sigma_k \sigma_l) \mu_B^2 / 2r^3$$
(3)

where  $\delta_{kl}$  is the Kronecker's delta,  $\sigma_k$  are cosines of the angles formed by the directions of the g components with the vector *r* joining the copper atoms. Tensor  $D_{dip}$  is not necessarily traceless.

To model the electron delocalization, the electron fractions  $\rho_i$ ,  $\rho_j$  are placed at a series of points numbered by i for one copper ion and by j for another copper ion and the contributions from each pair i,j are summed up:

$$(D_{dip})_{kl} = \sum_{i} \sum_{j} g_k g_l (\delta_{kl} - 3\sigma_k \sigma_l) \rho_i \rho_j \mu_B^2 / 2r_{ij}^3$$
(4)

 $r_{ij}$  now represents the distance from point i to point j and  $\sigma_k$  are the cosines of the angles formed by the directions of the *g* components with the vector  $r_{ij}$ .

#### The system of coordinates for calculation of the dipole-dipole interaction.

The direction of the  $g_z$  component was assumed to be perpendicular to the least-squares plane of the equatorial ligands of each copper atom, while the  $g_x$  direction dissected the projections of the Cu-O bonds

onto that plane. The direction of  $g_x$  defined in that way was only 3.6° away from the Cu-Cu direction. Tensor  $D_{dip}$  was calculated from formulas (3) or (4) above and was subsequently diagonalized.

### The Dipole-Dipole contribution

The point-dipole model (formula 3) gave the diagonal tensor components -98, 49, 59, all in units of  $10^{-4}$  cm<sup>-1</sup> in the coordinates defined above. Several equivalent sets of *D* and *E* may be obtained from formulas (1) depending on labeling the axes (i.e. which of the components is called  $D_{xx}$  etc.). To analyze the dipolar contribution alone it is convenient to consider the largest component as  $(D_{dip})_{zz}$ . Thus, the point-dipole model (formula 3) gave  $D_{dip}$ =-152. The model with delocalization (formula 4), placing <sup>1</sup>/<sub>4</sub> of an electron at the centre of each equatorial Cu-O and Cu-N bond gave  $D_{dip}$ =-142. Finally,  $D_{dip}$ =-118 was obtained placing 0.3 of an electron at the Cu-N bond centers and 0.2 at the Cu-O bond centers (all data in units of  $10^{-4}$  cm<sup>-1</sup>). It seems possible to approach the numerical value of the experimental *D* by using an appropriate delocalization scheme, but the EPR simulations favor positive sign for the experimental *D*.

#### The exchange contribution

From the experimental D=101, E=-6, values of the three diagonal **D** tensor components are calculated to be 68, -28 and -40, respectively. For simplicity, we average out the smaller components to obtain values 68, -34, -34. The powder EPR spectra only indicate that the distinguished **D** tensor component is perpendicular to the *Z* axis defined by the  $g_z$  direction, thus two sets:  $D_{xx}=68$ ,  $D_{yy}=-34$ ,  $D_{zz}=-34$  and  $D_{xx}=-34$ ,  $D_{yy}=68$ ,  $D_{zz}=-34$  are equally probable. The calculation of the dipole-dipole contribution (formula 3) gives  $(D_{dip})_{xx}=-98$ ,  $(D_{dip})_{yy}=49$ ,  $(D_{dip})_{zz}=59$  in the **g** system coordinates. Averaging out the smaller components we get  $(D_{dip})_{xx}=-98$ ,  $(D_{dip})_{yy}=54$ ,  $(D_{dip})_{zz}=54$  (the largest and negative dipolar component must lie along the Cu-Cu direction which in the **g** system coordinates we call X).

The exchange-induced tensor components  $(D_{ex})_{ii}$  are obtained by subtracting  $(D_{dip})_{ii}$  from the experimental  $D_{ii}$  and we obtain either

 $(D_{ex})_{xx} = 166, (D_{ex})_{yy} = -88, (D_{ex})_{zz} = -88$  or  $(D_{ex})_{xx} = 64, (D_{ex})_{yy} = 14, (D_{ex})_{zz} = -88$ These numbers should be treated as very rough estimates in view of the uncertainties in calculating the dipolar tensor  $\boldsymbol{D}_{dip}$ .