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Article

Reexamination of the Magnetic Properties of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ {dca = Dicyanamide; me_2pyz = Dimethylpyrazine}: Isolated Spin-$^1/_2$ Dimers versus Long-Range Magnetic Ordering

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The magnetic properties of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ have been reexamined. The extended structure of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ can be viewed in terms of $Cu_2(2,5\text{-}me_2pyz)^{4+}$ dimer units interconnected via $\mu_{1,5}$-dca ligands. The bulk magnetic susceptibility $\chi(T)$ and the isothermal $M(H)$ of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ are shown to be well described by an isolated dimer model. This finding was confirmed by carrying out a spin dimer analysis based on tight-binding calculations, which shows that the 2,5-me_2pyz ligand provides a substantial spin exchange interaction between the Cu^{2+} ions while the dca ligands do not.

1. Introduction

Transition metal dicyanamide (dca) complexes have received much interest from the molecular magnets community as well as others.[1] Such interest can be attributed to dca's coordination variability and particularly good Lewis basicity. Over the past year or so, several new bonding modes[2] have been identified although the $\mu_{1,5}$-mode seemingly appears on a more regular basis.[3]

Most synthetic efforts have apparently focused on Mn^{2+} as evidenced by the sheer number of reported crystal structures.[3] In this context, fewer studies have utilized Cu^{2+} ions, and a handful of molecular and polymeric structures are known.[4] The most interesting compounds, at least from a perspective of magnetism, are the α- and β-forms of $Cu(dca)_2(pyz)$[4a] that have three-dimensional (3D) and two-dimensional (2D) frameworks, respectively, and 3D $Cu_3(dca)_6(pym)_2$ {pym = pyrimidine} that consists of an intricate self-penetrating lattice.[4b]

Some of us previously reported the crystal structure and magnetic properties of $Mn(dca)_2(H_2O)_2(2,5\text{-}me_2pyz)_2$ that has a neutral 2D $Mn(dca)_2(H_2O)_2$ lattice. The 2,5-me_2pyz molecules are held in place by hydrogen bond interactions of the O−H···N type thus forming a 3D network.[5] The Fe^{2+} analogue has been prepared and characterized and found to be isostructural.[6] However, the Cu^{2+} analogue has a different

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(1) (a) Miller, J. S.; Manson, J. L. *Acc. Chem. Res.* **2001**, *34*, 563 and references therein. (b) Batten, S. R.; Murray, K. S. *Coord. Chem. Rev.* **2003**, *246*, 103 and references therein.

(2) (a) Marshall, S. R.; Incarvito, C. D.; Shum, W.; Rheingold, A. L.; Miller, J. S. *Chem. Commun.* **2002**, 3006. (b) Mohamadou, A.; van Albada, G. A.; Kooijman, H.; Wieczorek, B.; Spek, A. L.; Reedijk, J. *New J. Chem.* **2003**, *27*, 983.

(3) For example: (a) Manson, J. L.; Huang, Q.-z.; Lynn, J. W.; Koo, H.-J.; Whangbo, W.-H.; Bateman, R.; Otsuka, T.; Wada, N.; Argyriou, D. N.; Miller, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 162. (b) Manson, J. L.; Arif, A. M.; Incarvito, C. D.; Liable-Sands, L.; Rheingold, A. L.; Miller, J. S. *J. Solid State Chem.* **1999**, *145*, 369. (c) Dalai, S.; Mukherjee, P. S.; Zangrando, E.; Chaudhuri, N. R. *New J. Chem.* **2002**, *26*, 1185. (d) Escuer, A.; Mautner, F. A.; Sanz, N.; Vicente, R. *Inorg. Chem.* **2000**, *39*, 1668. (e) Escuer, A.; Mautner, F. A.; Sanz, N.; Vicente, R. *Inorg. Chim. Acta.* **2002**, *340*, 163. (f) Lin, H.-H.; Mohanta, S.; Lee, C. H.; Wei, H.-H. *Inorg. Chem.* **2003**, *42*, 1584. (g) Sun, B.-W.; Gao, S.; Ma, B.-Q.; Wang, Z.-M. *Inorg. Chem. Commun.* **2001**, *4*, 72. (h) Batten, S. R.; Jensen, P.; Kepert, C. J.; Kurmoo, M.; Moubaraki, B.; Murray, K. S.; Price, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 2987.

(4) (a) Jensen, P.; Batten, S. R.; Fallon, G. D.; Hockless, D. C. R.; Moubaraki, B.; Murray, K. S.; Robson, R. *J. Solid State Chem.* **1999**, *145*, 387. (b) Manson, J. L.; Gu, J.; Wang, H.-H.; Schlueter, J. A. *Inorg. Chem.* **2003**, *42*, 3950.

(5) Manson, J. L.; Schlueter, J. A.; Geiser, U.; Stone, M. B.; Reich, D. H. *Polyhedron* **2001**, *20*, 1423.

(6) Manson, J. L. Unpublished results.

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Table 1. X-ray Crystallographic Data for $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ Collected at 298 K

formula	$CuN_7C_7H_4$
fw	249.70
space group	$P2_1/n$
a, Å	7.4088(5)
b, Å	9.6805(8)
c, Å	13.6559(11)
β, deg	93.268(4)
V, Å^3	977.8(2)
Z	4
ρ_{calcd}, g/cm^3	1.696
λ, Å	0.71073
μ, mm^{-1}	2.21
$R(F)^a$	0.0571
$R_w(F)^b$	0.1568
GOF	1.068

^{a} $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w|F_o| - |F_c|^2/\Sigma w|F_o|^2]^{1/2}$.

structure with the composition $Cu_2(dca)_4(2,5\text{-}me_2pyz)$. During the course of our studies, the crystal structure and magnetic behavior of this compound were reported by Gao and coworkers, who concluded that the material undergoes a transition to long-range magnetic ordering below 5 K and a field-induced spin flop phase at ~70 kOe.[7] The present work found these conclusions to be incorrect. The crystal and electronic structures and the magnetic properties of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ are consistent with an isolated dimer model as we will describe herein.

2. Experimental Section

Synthesis. An aqueous solution containing $CuSO_4{\cdot}5H_2O$ (1 mmol, 0.2500 g) was slowly mixed with an aqueous solution that contained Nadca (2.1 mmol, 0.1872 g) and 2,5-me$_2$pyz (1 mmol, 0.1083 g) to give a pale blue solution. Upon standing at room temperature for ~2 weeks, well-formed green prisms of the title complex were obtained. These crystals were collected via suction filtration and air-dried for ~6 h (0.1944 g, 64% yield). Anal. Calcd (%) for $C_7H_4N_7Cu$: C, 33.67; H, 1.61; N, 39.27. Found: C, 33.73; H, 1.74; N, 39.12.

X-ray Crystallography. A green block measuring 0.35 × 0.20 × 0.15 mm^3 was selected for a structure determination and mounted on a Bruker X-ray diffractometer equipped with a CCD area detector. Approximately a hemisphere of data was measured to a resolution of 0.75 Å at 295 K. The detector frames were integrated by use of the program SAINT,[8] and the resulting intensities were corrected for absorption by Gaussian integration (SHELXTL program suite).[9] The SHELXTL program package was employed in the structure solution using direct methods, full-matrix least-squares refinement on F^2 (using all data), and some graphics. Additional graphics were created using *ORTEP3*.[10] Hydrogen atoms were located from difference maps, but in the final refinement their positions were calculated by employing a "riding" model. No correction for extinction was necessary. Additional details of the data collection are given in Table 1, and selected bond lengths and angles are listed in Table 2.

Magnetic Measurements. The temperature-dependence of the dc magnetization was measured using a Quantum Design MPMS-5S SQUID magnetometer over the temperature range 4−300 K. A powder sample was loaded into a gelatin capsule and mounted on the end of a Quantalloy rod. The sample was cooled to 4 K under zero-field conditions. Once the temperature became stable, the magnet was charged to 1 kOe, and data were collected upon warming to 300 K. Isothermal magnetization measurements were conducted on a Quantum Design PPMS 9-T ac/dc magnetometer equipped with the RSO option. The same sample was mounted on the end of a carbon fiber rod. The sample was quickly cooled to 2 K in a zero-applied field and allowed to equilibrate. The $M(H)$ curve was measured to 9 T using an extraction method. All magnetic data were corrected for diamagnetic contributions using Pascal's tables.

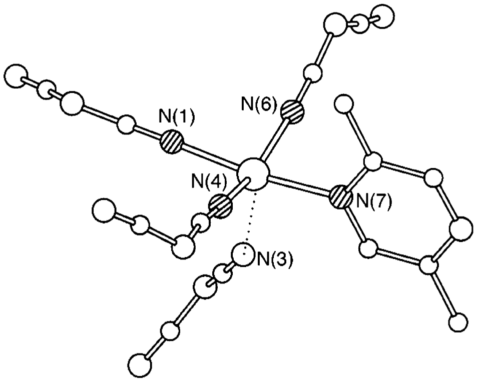

Figure 1. Schematic view of the five ligands surrounding a Cu^{2+} ion to form a square pyramidal spin monomer $[Cu(2,5\text{-}me_2pyz)(dca)_4]^{2-}$, **1**, in $Cu_2(dca)_4(2,5\text{-}me_2pyz)$. The N atoms occupying the basal sites are shown as shaded spheres.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $Cu_2(dca)_4(2,5\text{-}me_2pyz)$

Cu−N(1)	1.964(3)	N(1)−C(1)	1.126(5)
Cu−N(3)	2.173(4)	N(2)−C(1)	1.275(6)
Cu−N(4)	1.964(4)	N(2)−C(2)	1.289(5)
Cu−N(6)	1.986(3)	N(3)−C(2)	1.129(5)
Cu−N(7)	2.052(3)	N(7)−C(5)	1.343(4)
		N(7)−C(7)	1.335(4)
N(1)−Cu−N(3)	92.6(2)	C(1)−N(1)−Cu	173.0(4)
N(4)−Cu−N(1)	90.6(2)	C(2)−N(3)−Cu	146.3(4)
N(3)−Cu−N(4)	101.8(2)	C(3)−N(4)−Cu	177.3(4)
N(1)−Cu−N(7)	172.4(2)	C(1)−N(2)−C(2)	128.2(4)
N(3)−Cu−N(7)	94.9(1)	N(2)−C(2)−N(3)	169.2(5)
N(4)−Cu−N(6)	155.6(2)	N(2)−C(1)−N(1)	168.5(5)
N(6)−Cu−N(7)	87.6(1)		

3. Results and Discussion

Crystal Structure. The structure has been previously reported,[7] so we describe only the pertinent features of the structure that are essential for our discussion. As shown in Figure 1, each Cu^{2+} ion is surrounded by five ligands to form a distorted square-pyramidal coordination geometry. This unit $[Cu(2,5\text{-}me_2pyz)(dca)_4]^{2-}$ (**1**) contains one unpaired spin and is therefore a spin monomer. The N atoms of three dca's and one 2,5-me$_2$pyz occupy the basal positions of the square pyramid, and the apical position is occupied by the N atom of one dca. The dca ligand uses the N sp lone pairs for coordination while the 2,5-me$_2$pyz uses the N sp^2 lone pairs for coordination. The Cu−N$_{basal}$ distances with the dca ligands are similar, i.e., Cu−N(1) = 1.964(3) Å, Cu−N(4) = 1.964(4) Å, and Cu−N(6) = 1.986(3) Å, and that with

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(7) Yeung, W.-F.; Gao, S.; Wong, W. T.; Lau, T. C. *New J. Chem.* **2002**, *26*, 523.

(8) *SAINT, Version 5.00, Data Integration Software*; Bruker AXS, Inc.: Madison, WI, 1999.

(9) *SHELXTL, Version 5.0, Structure Solution and Refinement Software*; Bruker AXS, Inc.: Madison, WI, 1996.

(10) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

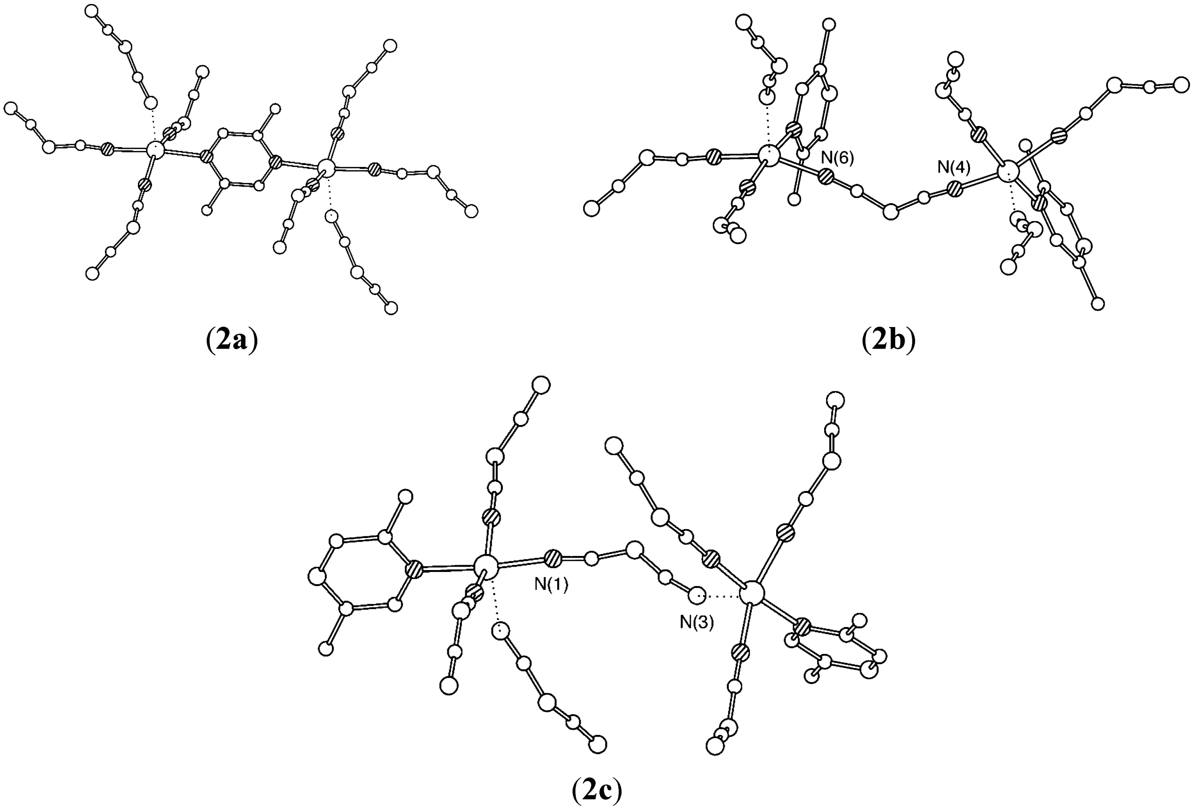

Figure 2. Schematic views of the three types of bridging between adjacent Cu^{2+} ions in $Cu_2(dca)_4(2,5\text{-}me_2pyz)$. The N atoms occupying the basal sites were shown by shading: (a) the 2,5-me$_2$pyz bridging leading to the spin dimer $[Cu_2(2,5\text{-}me_2pyz)(dca)_8]$,$^{4-}$ **2a**; (b) the dca bridging leading to the spin dimer $[Cu_2(2,5\text{-}me_2pyz)_2(dca)_7]^{3-}$, **2b**; (c) the dca bridging leading to the spin dimer $[Cu_2(2,5\text{-}me_2pyz)_2(dca)_7]^{3-}$, **2c**.

2,5-me$_2$pyz is slightly longer, i.e., Cu−N(7) = 2.052(3) Å. The Cu−N$_{apical}$ distance is substantially longer, i.e., Cu−N(3) = 2.173(4) Å. Due to the deformation of the basal plane, the N−Cu−N bond angles within the basal plane deviate from 90°, while the *trans*-N−Cu−N bond angles deviate from 180° [i.e., N(1)−Cu−N(7) = 172.4(2)° and N(4)−Cu−N(6) = 155.6(2)°].

All adjacent Cu^{2+} ions are linked together via three types of bridges where the shortest Cu•••Cu separation is 6.870 Å across the 2,5-me$_2$pyz bridge and much longer across the dca bridges (8.127 and 8.346 Å). Figure 2a shows the bridging by a 2,5-me$_2$pyz ligand to form the dimer unit $[Cu_2(2,5\text{-}me_2pyz)(dca)_8]^{4-}$ (**2a**), in which the two N atoms of the bridging 2,5-me$_2$pyz occupy the basal positions of the square pyramids. Figure 2b shows the bridging by a dca ligand to form the dimer unit $[Cu_2(2,5\text{-}me_2pyz)_2(dca)_7]^{3-}$ (**2b**), in which the two cyano N atoms of the bridging dca occupy the basal positions of the square pyramids. Figure 2c shows an alternative bridging by a dca ligand to form the dimer unit $[Cu_2(2,5\text{-}me_2pyz)_2(dca)_7]^{3-}$ (**2c**), in which one cyano N atom of the bridging dca occupies a basal position of one square pyramid while the other cyano N atom of the bridging dca occupies an apical position of the other square pyramid. The large Cu•••Cu separations imposed by the long bridging ligands lead to a 3D structure that consists of 2-fold interpenetrated frameworks, Figure 3.

Magnetic Properties. The temperature dependence of the magnetic susceptibility has been measured between 2 and 300 K and is shown in Figure 4. Upon cooling from 300 K, $\chi(T)$ gradually increases until reaching a maximum value of 0.049 emu/mol at 9.3 K. It then decreases smoothly upon cooling further to 4 K. The broad maximum in $\chi(T)$ is likely due to short-range antiferromagnetic interactions between nearest-neighbor spin-$^1/_2$ Cu^{2+} sites. A fit of the $\chi(T)$ data to the Curie−Weiss expression above 20 K yielded g = 2.168(1) and $\theta = -5.2(1)$ K. The 2,5-me$_2$pyz ligand provides the shortest bridging between adjacent Cu^{2+} ions while $\mu_{1,5}$-bonded Cu−dca−Cu bridges mediate very weak exchange coupling. Thus, we chose to fit the susceptibility using the Bleaney−Bowers expression ($H = -JS_1 \cdot S_2$) for an isolated spin-$^1/_2$ dimer.[11] As can be seen in Figure 4, an excellent fit is obtained giving g = 2.173(5) and $J = -7.31(2)$ K. For the sake of completeness, the fit also included a mean-field

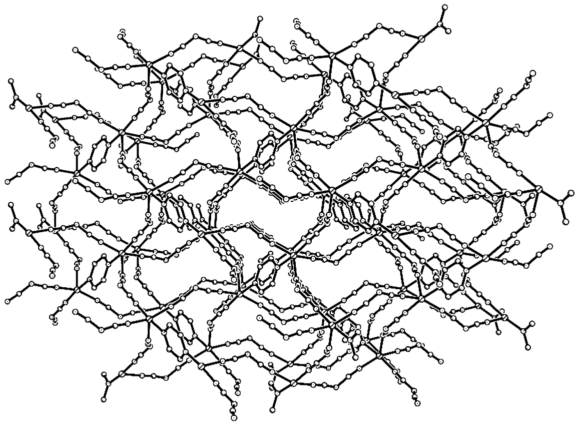

Figure 3. Two-fold interpenetrating 3D network for $Cu_2(dca)_4(2,5\text{-}me_2pyz)$. Methyl groups have been omitted for clarity.

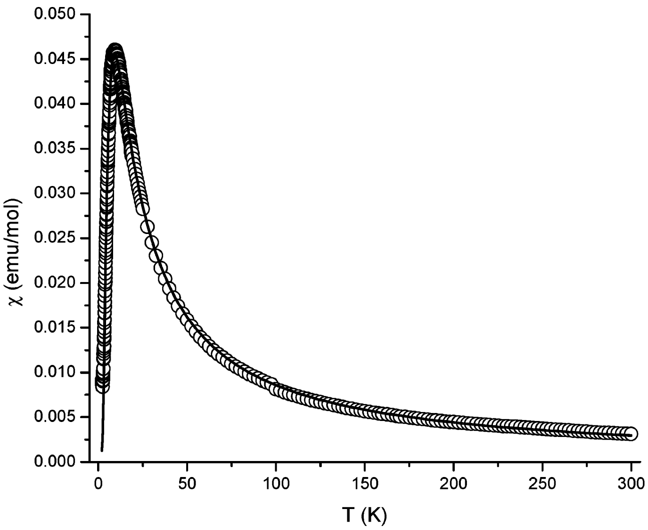

Figure 4. Temperature variation of the molar magnetic susceptibility (○) for $Cu_2(dca)_4(2,5\text{-}me_2pyz)$. The solid line represents the theoretical fit to the Bleaney−Bowers expression for a coupled $S = {}^1/_2$ Cu^{2+} dimer that also incorporates a mean-field correction term as described in the text.

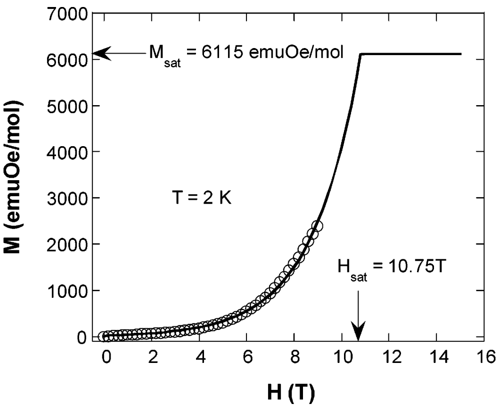

Figure 5. Isothermal magnetization data (○) acquired at 2 K for $Cu_2(dca)_4(2,5\text{-}me_2pyz)$. The solid line delineates the theoretical fit expected for an isolated $S = {}^1/_2$ Cu^{2+} dimer as described in the text.

correction term, i.e., zJ', which yielded a negligibly small value of $-0.08(1)$ K.[12] This shows that $\mu_{1,5}$-bonded Cu−dca−Cu bridges mediate very weak exchange coupling.

The isothermal magnetization, $M(H)$, acquired at 2 K initially rises slowly for lower fields and then increases much more rapidly above ~6 T (Figure 5). Expectedly, the data do not show evidence for reaching a saturation magnetization up to 9 T. These data further corroborate our description of the magnetic susceptibility of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ using an isolated dimer model. It can be seen that an isolated dimer model (solid line in Figure 5) using the same parameters obtained from the $\chi(T)$ fit yields very good agreement up to the highest attainable field. We have extrapolated the calculated $M(H)$ to higher field values to demonstrate the expected behavior. From this, we expect a saturated magnetic state to occur at 10.75 T and reach a value of 6115 emu Oe/mol; and this expectation is fully consistent with our model.

Spin Dimer Analysis. In understanding magnetic properties of a magnetic solid, it is necessary to estimate the relative strengths of the spin exchange interactions associated with various spin exchange paths on the basis of either first principles[13] or qualitative[14] electronic structure calculations for various spin dimers (i.e., structural units containing two spin sites) of a magnetic solid under consideration. The three possible spin dimers of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ are **2a**, **2b**, and **2c**. In general, a spin exchange parameter J is written as $J = J_F + J_{AF}$, where the ferromagnetic term J_F (>0) is small, so that the spin exchange becomes ferromagnetic (i.e., $J > 0$) when the antiferromagnetic term J_{AF} (<0) is negligibly small in magnitude. Spin exchange interactions are primarily antiferromagnetic (i.e., $J < 0$) and can be discussed by focusing on the antiferromagnetic term J_{AF}. If each spin site of a magnetic solid contains one unpaired electron, then the antiferromagnetic term J_{AF} is written as $J_{AF} = -(\Delta e)^2/U_{eff}$, where Δe is the energy split between the two singly filled levels of a spin dimer, and U_{eff} is the effective on-site repulsion. For a given magnetic solid, the U_{eff} value is nearly constant so that the trend in J_{AF} is well approximated by that in the corresponding $-(\Delta e)^2$.[14] The Δe values determined for the spin dimers **2a**, **2b**, and **2c** using extended Hückel tight binding calculations[15−17] show that the Δe value is substantial in the spin dimer **2a** linked by the $2,5\text{-}me_2pyz$ bridge but is negligible for the spin dimers **2b** and **2c** linked by the dca bridge. Consequently, the strongly interacting spin units within $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ are the spin dimers **2a** that are isolated and do not interact, at least to a first approximation. This explains why the magnetic susceptibility of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ is well described by an isolated dimer model.

The magnetic orbital (i.e., the singly occupied orbital) of the spin monomer **1** has the contribution of the Cu $x^2 - y^2$ orbital in the basal plane. As depicted in Figure 6, the two Cu $d_{x^2-y^2}$ orbitals of the spin dimer **2a** overlap well with the n_+ and n_- orbitals of $2,5\text{-}me_2pyz$. The n_- level lies considerably lower in energy than the n_+ level due to a through-bond interaction.[18] Thus, the extent of their interactions with the Cu $d_{x^2-y^2}$ orbitals are different, leading to a substantial energy difference between the two singly occupied orbitals of the spin dimer and consequently a strong antiferromagnetic coupling between the two Cu^{2+} ions. In the spin dimer **2b**, the two Cu $d_{x^2-y^2}$ orbitals interact weakly through the bridging dca ligand even though both cyano N atoms of the bridging dca occupy the basal positions of the square pyramids. Unlike the case of the two N sp^2 lone pairs

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(11) (a) Bleaney, B.; Bowers, K. *Proc. R. Soc. London, Ser. A.* **1954**, *214*, 451. (b) Bleaney, B.; Bowers, K. *Philos. Mag.* **1952**, *43*, 372.

(12) Ginsberg, A. P.; Lines, M. E. *Inorg. Chem.* **1972**, *11*, 2289.

(13) Illas, F.; Moreira, I. de P. R.; de Graaf, C.; Barone, V. *Theor. Chem. Acc.* **2000**, *104*, 265 and references therein.

(14) For a recent review, see: Whangbo, M.-H.; Koo, H.-J.; Dai, D. *J. Solid State Chem.* **2003**, *176*, 417.

(15) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(16) Our calculations were carried out by employing the CAESAR and SAMOA program packages (Dai, D.; Ren, J.; Liang, W.; Whangbo, M.-H. http://chvamw.chem.ncsu.edu/).

(17) The double-ζ Slater type orbitals were used for the Cu 3d orbital, and the single-ζ Slater type orbitals were used for all other atomic orbitals. The H_{ii} value of Cu 3d was raised by 1.5 eV compared with the usual value. The Δe value was calculated to be 0.82 eV for **2a**, but it is zero for **2b** and **2c**.

(18) Hoffmann, R., *Acc. Chem. Res.* **1971**, *4*, 1.

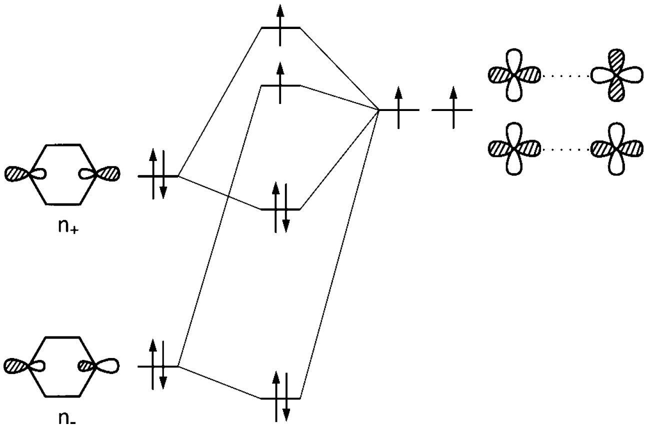

Figure 6. Schematic orbital interaction diagram showing the interaction between the n_+ and n_- orbitals of 2,5-me_2pyz with the two Cu $d_{x^2-y^2}$ orbitals in the spin dimer **2a**.

of 2,5-me_2pyz, the two N sp lone pairs of a dca ligand do not interact through the bonds so that their energy levels are not split; consequently, the two singly occupied orbitals of the spin dimer **2b** do not split. In the spin dimer **2c**, the two Cu $d_{x^2-y^2}$ orbitals cannot interact through the bridging dca ligand because one cyano N atom of the bridging dca occupies the apical position of one square pyramid. Thus, the two Cu^{2+} ions of **2b** and **2c** have a negligible antiferromagnetic interaction.

4. Concluding Remarks

Adjacent Cu^{2+} ions of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ are linked by three kinds of bridging modes, namely, the 2,5-me_2pyz bridge shown in **2a** and the two different dca bridges shown in **2b** and **2c**. Our spin dimer analysis shows that the 2,5-me_2pyz bridge provides a substantial spin exchange interaction and that the dca bridges do not. Thus, the magnetic susceptibility of $Cu_2(dca)_4(2,5\text{-}me_2pyz)$ is very well described by an isolated dimer model with $g = 2.173(5)$ and $J = -7.31(2)$ K, and a mean-field correction, zJ', has a negligibly small value of $-0.08(1)$ K. The isothermal $M(H)$ is also well described by an isolated dimer model.

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