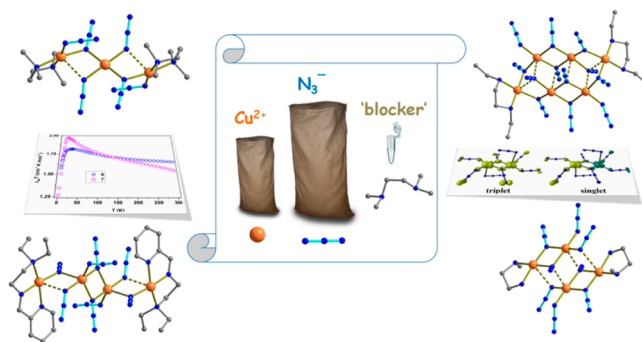


## Versatility of Azide in Serendipitous Assembly of Copper(II) Magnetic Polyclusters

SANDIP MUKHERJEE AND PARTHA SARATHI MUKHERJEE\*  
*Department of Inorganic and Physical Chemistry, Indian Institute of Science,  
Bangalore-560012, India*

RECEIVED ON FEBRUARY 26, 2013

### CONSPECTUS



Engineering at the molecular level is one of the most exciting new developments for the generation of functional materials. However, the concept of designing polynuclear extended structures from bottom up is still not mature. Although progress has been made with secondary building units (SBUs) in metal organic frameworks (MOFs), the control seems to be just an illusion when it comes to bridging ligands such as the azide ion. When we say that the azido ligand is versatile in its bridging capabilities, what we mean is that it would be difficult to predict or control its bridging properties. However, this kind of serendipity is not always bad news. For example, scientists have shown that the azido ligand can mediate magnetic exchanges between paramagnetic metals in a predictable fashion (usually depending upon the bonding geometries). Therefore, it is a well-respected ligand in polynuclear assemblies. Serendipitous assemblies offer new magnetic structures that we may not otherwise even think about synthesizing.

The azido ligand forms a variety of complexes with copper(II) using different blocking amines or pyridine based ligands. Its structural nature changes upon changing the substitution on amine, as well as the amount of blocking ligand. In principle, if we take any of these complexes and provide more coordination sites to the bridging azido ligands by removing a fraction of the blocking ligands, we can get new complexes with intricate structural networks and therefore different magnetic properties with the same components as used for the parent complex. In this Account, we mainly discuss the development of a number of new topological and magnetic exchange systems synthesized using this concept.

Not all of these new complexes can be grouped according to their basic building structures or even by the ratio of the metal to blocking ligand. Therefore, we divided the discussion by the nuclearity of the basic building structures. Some of the complexes with the same nuclearities have very similar or even almost identical basic structures. However, the way these building units are joined together (by the azido bridges) to form the overall extended structures differ almost in every case. The complexes having the  $\text{Cu}_6$  core are particularly interesting from a structural point of view. Although they have almost identical basic structures, some of them are extended in three dimensions, but two of them are extended in two dimensions by two different bridging networks. In the complexes having linear  $\text{Cu}_4$  basic units, we find that using similar ligands does not always give the same bridging networks even within the basic building structures.

These complexes have also enriched the field of molecular magnetism. One of the complexes with a  $\text{Cu}_3$  building unit has provided us with the opportunity to study the competing behavior of two different kinds of magnetic exchange mechanism (ferromagnetic and antiferromagnetic) acting simultaneously between two metal ions. Through density functional theory calculations, we showed how they work independently and their additive nature to produce the overall effect. The exciting methodology for the generation of copper(II) polyclusters presented in this Account will provide the opportunity to explore analogous serendipitous assembly of diverse structures with interesting magnetic behavior using other transition metal ions having more than one unpaired electrons.

## Introduction

The word Serendipity was introduced in the English language by Horace Walpole, who (1754) manufactured it upon the title of the Persian fairy tale “*The Three Princes of Serendip*”, in which the heroes “were always making discoveries, by accidents and sagacity, of things they were not in quest of.” Modern inorganic chemists involved in the “synthesis of serendipitous assemblies” are however quite happy to take their chances in the quest of their choices. Their motivation lies in the fact that the hugely successful retrosynthetic principles and general preparative processes that have profound effects in synthetic organic chemistry, as well as the pharmaceutical industry, have no analogous protocols for achieving the logical synthesis of extended structures containing metals or for prediction of their topology.<sup>1,2</sup> Although great progress have been achieved in constructing metal organic frameworks (MOFs) by using secondary building units (SBUs), directed synthesis is still a great challenge because the assembly progress is highly influenced by several factors, such as the metal/ligand nature, solvents, templates, and counterions.<sup>1–7</sup> In serendipitous assembly, unexpected structural topologies can be obtained by using one or several bridging ligands and coligands in a variety of combinations most of which are otherwise difficult to predesign.<sup>8–10</sup>

A large collection and class of bridging anionic ligands have been featured in the field of coordination polymers. Along with the ubiquitous carboxylates, the three-atom azide ion has remained a very popular choice for the last two decades.<sup>11–20</sup> The three-atomic pseudohalide (azide) provides special prospects for its intriguing variety of bridging modes, some of which are often seen to coexist in the same complex (Scheme 1).

For paramagnetic metal azido complexes, the end-to-end (EE) azido bridging mode generally transmits antiferromagnetic interaction (if the M–NNN–M torsion angle is near 90°, then ferromagnetic exchange is expected),<sup>12</sup> while the behavior of the end-on (EO) azido mode is very intricate. In the widely studied copper(II)-azido systems, it is now well established that the magnetic interaction between the copper(II) ions is ferromagnetic if the Cu–N<sub>EO</sub>–Cu angle is below the critical angle of ~108° (however the density functional theory (DFT) analysis suggests a value of ~104°)<sup>16</sup> and antiferromagnetic above it.<sup>11–20</sup> It should however be noted that similar studies on other transition metal azido complexes, especially for nickel and manganese, also provided many insights into the magnetic exchange mechanism.<sup>12</sup>

To effectively use the full potential of the azide ion as a bridging ligand, two strategies are generally used. First, extra

equivalents of azide ion can be used than the charge of the metal concerned allows, by introducing a secondary cation (tetraalkylammonium and monovalent alkali metals have been used).<sup>21,22</sup> On the other hand, decreasing the proportion of the blocking coligands can open up more coordinating sites on the metal atoms for the azide ions. In this Account, we present our recent efforts in developing the later strategy for neutral copper(II)-azido systems using varied proportions of a multitude of blocking ligands with different denticity.<sup>23–29</sup> This relatively new strategy has helped us to obtain a large number of copper(II)-polyclusters with complex structures and magnetic behavior including structural transformations.

## Simple Strategy: Complex Structures

Typically, these complexes are obtained from the reactions of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O or CuCl<sub>2</sub>·2H<sub>2</sub>O and lower than 1 mol equivalent of the blocking ligands with an excess of NaN<sub>3</sub> in a MeOH/H<sub>2</sub>O mixture, and the slow evaporation of the resulting mixture at room temperature affords good quality crystals for subsequent studies. Using an excess of NaN<sub>3</sub> normally ensures the prevention of the immediate precipitation of Cu(N<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O, allowing the crystallization of multi-dimensional compounds via self-assembly of the smaller units. The complexity of these kinetic crystallization methods revealed itself remarkably in the case of ethylenediamine ligand, for which an initially formed complex with 0.2 mol equivalent of the diamine slowly transformed to a complex with 1 equiv of the diamine via an intermediate complex, when left in the mother liquor (Scheme 2).<sup>23</sup>

The power of this new concept or more appropriately the methodology can be appreciated by the fact that only in the last 3–4 years several new structural topologies were obtained.<sup>23–36</sup> Most of these complexes have simple building units, but interestingly their arrangements in the higher dimensions are not necessarily identical. Therefore, we will group only some of the representative complexes based on their nuclearity in the basic units, and discuss the various structural and magnetic consequences of their extended arrangements.

## Cu<sub>3</sub> Building Units

When we isolated the complex [Cu<sub>3</sub>(tmen)<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>] and found that the three copper(II) centers were held together by double end-on azido bridges,<sup>24</sup> at least two similarly bridged linear trinuclear complexes were already known (Figure 1).<sup>37,38</sup> But unlike these two, our complex had a novel feature that may not be that important from a structural point of view, but

SCHEME 1. Common Bridging Modes of the Azido Ligand

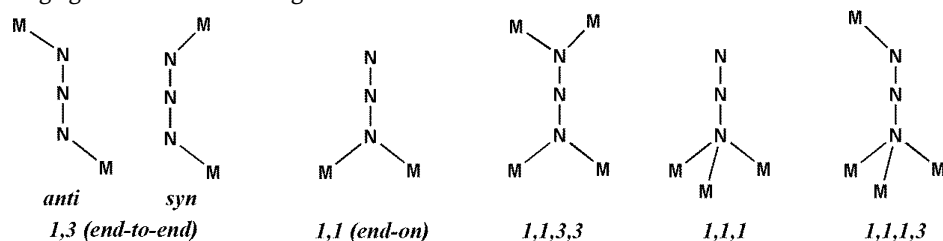
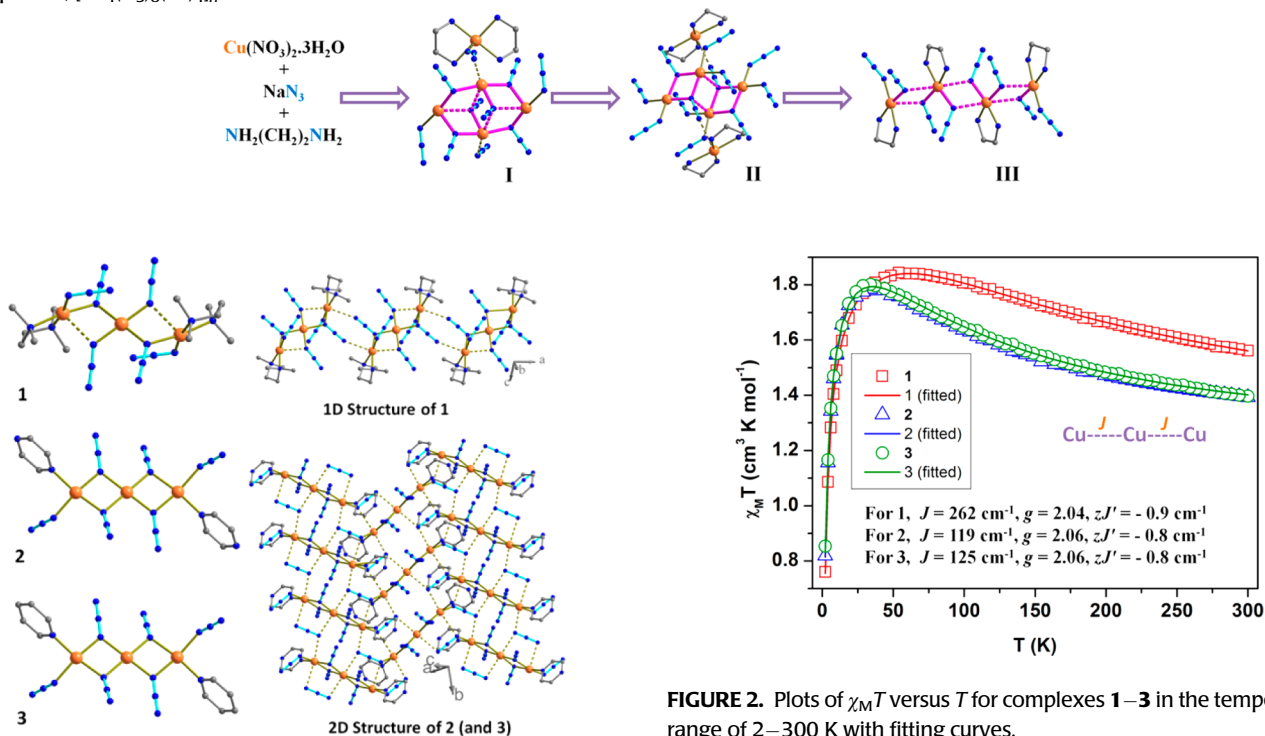
SCHEME 2. Structural Transformation in the Basic Building Unit of Complex I,  $[\text{Cu}_5(\text{N}_3)_{10}(\text{en})_2]_n$ , to Complex II,  $[\text{Cu}_6(\text{N}_3)_{12}(\text{en})_4]_n$ , and to Finally Complex III,  $[\text{Cu}_4(\text{N}_3)_8(\text{en})_4]_n$ 

FIGURE 1. Structures of the complexes **1**, **2** and **3** with trinuclear basic unit. **2** and **3** are essentially iso-structural. [Color codes: orange = Cu, blue = N, gray = C; H atoms are removed for clarity].

when considering the magnetic behavior it had a profound effect. As we have already mentioned that the sign and the magnitude of the magnetic exchange between copper atoms bridged by end-on azido groups depend primarily on the bridging angle, it was remarkable that in **1** the two azido groups exerted the bridging angle on either side of the cutoff angle ( $108^\circ$ ). While one of these angles is just above the cutoff point ( $108.25^\circ$ ), the other one is considerably shorter ( $92.72^\circ$ ). The experimental susceptibility data cannot provide the necessary information to assign different exchange parameters for the two different azido bridges joining the same pair of metal atoms, so the fitting only provides an average estimation of the exchange. The fitting equation was obtained by using

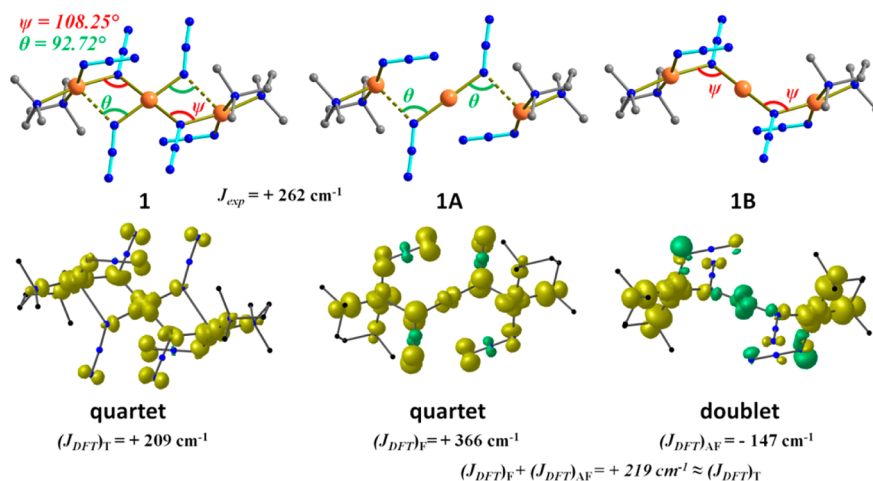
FIGURE 2. Plots of  $\chi_M T$  versus  $T$  for complexes **1–3** in the temperature range of 2–300 K with fitting curves.

the conventional Hamiltonian for centrosymmetric trinuclear copper(II) ( $S = 1/2$ ) spin-exchange system:

$$H = -J(S_1 S_2 + S_2 S_3)$$

Intercluster interaction ( $zJ'$ ) and temperature independent paramagnetic correction were also used to analyze the data, and the best fit parameters were found to be  $J = 262 \text{ cm}^{-1}$ ,  $zJ' = -0.9 \text{ cm}^{-1}$ ,  $g = 2.04$ , and  $\alpha_{(\text{TP})} = 0.0013 \text{ cm}^3 \text{ mol}^{-1}$ .

It has been argued that when multiple pathways (bridges) are available for magnetic exchange between two ions, the overall effect arises essentially from the algebraic sum of the individual exchanges. Our complex provided the perfect opportunity to investigate this assumption. So we carried out DFT calculations on the geometries obtained from the crystallographic data, to estimate the value of the exchange parameter by calculating the single-point energies of the two



**FIGURE 3.** Model structures used for DFT studies (top) and the spin density maps of the calculated spin ground states (quartet for **1** and **1A**; doublet for **1B**) for these models. Positive and negative spin populations are represented as yellow and green surfaces, respectively. The isodensity surfaces correspond to a value of  $0.003e/b^3$ .

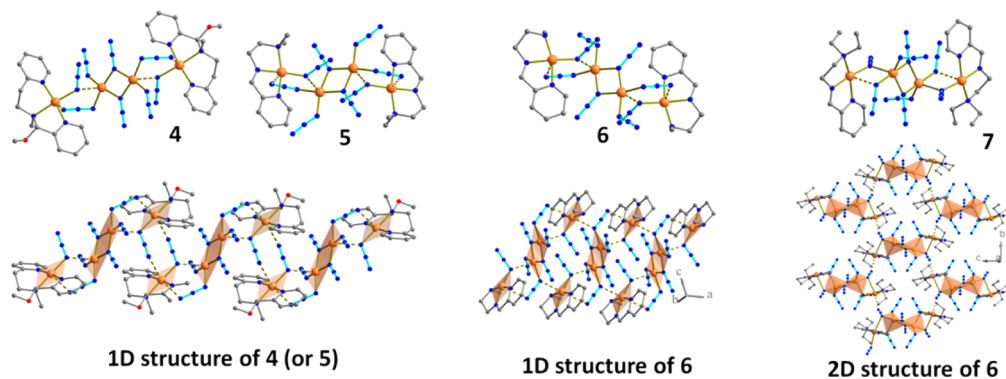
spin states arising from three  $S = 1/2$  ions, namely, doublet and quartet. Along with the parent complex (model **1**) we also measured the  $J$  values, by selectively removing the AF and F-azido groups (model **1A** and **1B**) to get an idea about their individual contributions (Figure 3). This process of removing azido groups does change the overall energies of the individual spin states, but we are mainly concerned with the change in the relative energies of the spin states which is the measure of the exchange coupling constant,  $J$ . The calculated  $J$  value for **1**,  $J_T = 209 \text{ cm}^{-1}$ , is somewhat lower in magnitude compared to the experimental fitted value of  $262 \text{ cm}^{-1}$  (Figure 2). However, when the  $J$  values obtained for **1A** ( $J_F = 366 \text{ cm}^{-1}$ ) and **1B** ( $J_{AF} = -147 \text{ cm}^{-1}$ ) are added, they are almost same as that calculated for **1** ( $J_F + J_{AF} = 219 \approx J_T$ ), showing that the assumption of additivity of the exchange pathways is roughly accurate. It should be noted that although the cutoff angle for ferromagnetic and antiferromagnetic interactions is taken as  $108^\circ$  (experimental average), it has been shown by DFT analysis that this cutoff angle is  $\sim 104^\circ$ .<sup>16</sup> Therefore, the DFT analysis overestimates the magnitude of the  $J_{AF}$  contribution. However, this is compensated by the overestimation of the ferromagnetic contribution as well. Therefore, the overall estimation of the exchange parameter ( $J_F + J_{AF}$ , or  $J_T$ ) is reasonably acceptable. The fact that the real complexes are not discrete entities as they are modeled, but are quite complicated in their overall structures, and that the flexibility of the ligands allows minute structural changes with temperature, implies that the calculated exchange constants are only qualitative, but nevertheless, they do provide some insights into the possible exchange mechanisms in these systems.

We isolated two more trinuclear complexes with monodentate blocking ligands [pyrazine (**2**) and pyridine (**3**)] with identical structures.<sup>25</sup> The coligands being monodentate (and used in the same molar ratio as in **1**) opened two more sites per trinuclear cluster unit, and so the overall structures of these two complexes are 2D. Unlike the case of **1**, in **2** and **3**, the double end-on azido bridges linking the adjacent copper atoms within the trinuclear units are symmetrical with all of the bridging angles being very close to  $100^\circ$  and all the bonds involved in the bridging being short equatorial/basal bonds. Therefore, moderately strong ferromagnetic exchange is expected for these complexes, which was confirmed by data fitting ( $119 \text{ cm}^{-1}$  for **2** and  $125 \text{ cm}^{-1}$  for **3**).

### Cu<sub>4</sub> Building Units

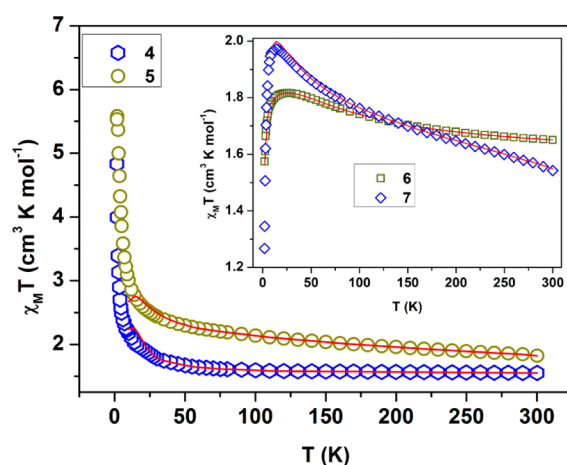
Copper(II) generally forms four to six bonds; so use of multidentate ligands (denticity  $\geq 3$ ) may not seem to be a smart choice. Still several very interesting complexes were isolated using these ligands in smaller molar quantities. The first such complex was obtained rather accidentally by Zhou et al. in 2004, in which, although the reaction was carried out with equimolar quantities of copper(II) and diethylenetriamine, the resulting trinuclear complex had in its basic structure one copper(II) atom lacking the chelate.<sup>38</sup> More recently, Lin et al. have synthesized copper(II)-azido neutral assemblies using polyamine ligands such as triethylenetetramine, diethylenetriamine, and pentamethyldiethylenetriamine hydrothermally using triethyl orthoformate as an acidic buffer to suppress the effective concentrations of these chelating ligands.<sup>34</sup>

But in our group we were able to use a more direct approach by using tridentate ligands obtained from the condensation of



**FIGURE 4.** Ball and stick view of the basic and overall structures of the complexes **4–7**. Color codes: orange = Cu, blue = N, red = O, and gray = C. The shaded planes shown in brown represent the polyhedra extended by the coordinated nitrogen atoms (with bond lengths  $< 2.2 \text{ \AA}$ ) at the metal centers.

2-pyridinecarboxaldehyde with diamines having only one primary amine (while the other side is blocked by alkyl substituents).<sup>27,29</sup> Isolation of these ligands from the condensation reactions was not found to be necessary, so we tried out a reaction, rather boldly, by mixing the aldehyde with a secondary amine [2-{2-(methylamino)ethyl}pyridine] and then introducing this mixture in a water–methanolic solution of copper(II) and excess of azide. The result was both surprising and encouraging, as we isolated a complex of formula  $[\text{Cu}_4(\text{L}^1)_2(\text{N}_3)_8]_n$  (**4**) which had two out of the four copper atoms in the basic structure lacking any “blocker” (which was our primary goal), while the other two copper(II) atoms were chelated by a hemiaminal ether (the first such compound to be trapped in a metal complex). Two other complexes of the formula  $[\text{Cu}_4(\text{L}^2)_2(\text{N}_3)_8]_n$  (**5**) and  $[\text{Cu}_4(\text{L}^3)_2(\text{N}_3)_8]_n$  (**6**) with almost identical tetranuclear cluster units were isolated using similar ligands derived from *N,N*-dimethylethylenediamine ( $\text{L}^2$ ) and *N*-methylethylenediamine ( $\text{L}^3$ ). The most important structural feature of these three complexes is the presence of both end-on and end-to-end bridging between the peripheral copper(II) atoms. The rarity of this kind of bonding is due to the fact that, generally, the EO mode brings two bridged copper(II) atoms very close ( $\sim 3 \text{ \AA}$ ), while the three-atom EE mode keeps the metals at greater separations ( $\sim 5 \text{ \AA}$ ). So, the EO-bridging necessitates at least one longer bond (axial/apical) and the bridging angle also inflates. For these complexes, the peripheral Cu–Cu distance was found to be  $\sim 4.2 \text{ \AA}$  and the EO bridging angles for **4**, **5**, and **6** were found to be  $131.1^\circ$ ,  $134.7^\circ$ , and  $137.2^\circ$ , respectively. All three complexes have an overall 1D structure. However, interestingly, the linking patterns among the tetranuclear building clusters differ in **6**. In complexes **4** and **5**, the tetranuclear units are joined in a head-to-tail manner, while in **6** the units are stacked laterally (Figure 4). Another very interesting change in structure is observed when  $\text{L}^2$  is replaced by  $\text{L}^4$  (differing only in their two alkyl



**FIGURE 5.** Plots of  $\chi_M T$  versus  $T$  for complexes **4–7** in the temperature range of 2–300 K. The red lines indicate the fitting.

substituents, Me and Et). The basic structure of the resulting complex  $[\text{Cu}_4(\text{L}^4)_2(\text{N}_3)_8]_n$  (**7**) is still tetranuclear, and the bridging between the central metal atoms is identical, but the bridging between the peripheral metal atoms changes remarkably to the double end-on mode (decreasing the Cu–Cu distance to  $\sim 3.39 \text{ \AA}$ ), which also changes the overall structure with an increase in the dimensionality (2D).

The magnetic exchange in the basic centrosymmetric core of these four complexes can be modeled as  $\text{Cu}(S_1) - J_1 - \text{Cu}(S_2) - J_2 - \text{Cu}(S_3) - J_1 - \text{Cu}(S_4)$  (Figure 5). The fitting values for the exchange coupling constants using the interacting tetranuclear model for **4**, **5**, and **7**, and noninteracting model for **6**, have been given in Table 1. For the complexes **4–6**, the Cu–N<sub>EO</sub>–Cu bond angles for the two central metal atoms are well below the cutoff angle  $108^\circ$  and also all the bridging bonds are “short”. So moderately strong ferromagnetic interactions are expected for this pair of copper(II) ions. The very small magnitude for  $J_1$  can be justified by the fact that both the bridging between the peripheral copper

TABLE 1. Summary of the Features of the Complexes Discussed in This Account

complex	formula	no. of sites blocked per cu	structure <sup>a</sup>	magnetic properties <sup>b</sup>		ref
				$J_{\text{EXP}}$ (cm <sup>-1</sup> )	$J_{\text{DFT}}$ (cm <sup>-1</sup> )	
<b>1</b>	[Cu <sub>3</sub> (tmen) <sub>2</sub> (N <sub>3</sub> ) <sub>6</sub> ] <sub>n</sub>	1.33	1D (a)	+262	+209	24
<b>2</b>	[Cu <sub>3</sub> (pyz) <sub>2</sub> (N <sub>3</sub> ) <sub>6</sub> ] <sub>n</sub>	0.67	2D (b)	+119	+148	25
<b>3</b>	[Cu <sub>3</sub> (py) <sub>2</sub> (N <sub>3</sub> ) <sub>6</sub> ] <sub>n</sub>	0.67	2D (b)	+125	+214	25
<b>4</b>	[Cu <sub>4</sub> (L <sup>1</sup> ) <sub>2</sub> (N <sub>3</sub> ) <sub>8</sub> ] <sub>n</sub>	1.50	1D (c)	-2.2	-32	27
				+55	+106	
<b>5</b>	[Cu <sub>4</sub> (L <sup>2</sup> ) <sub>2</sub> (N <sub>3</sub> ) <sub>8</sub> ] <sub>n</sub>	1.50	1D (c)	-1.4	-23	27
				+39	+57	
<b>6</b>	[Cu <sub>4</sub> (L <sup>3</sup> ) <sub>2</sub> (N <sub>3</sub> ) <sub>8</sub> ] <sub>n</sub>	1.50	1D (d)	-0.7	-4	29
				+65	+84	
<b>7</b>	[Cu <sub>4</sub> (L <sup>4</sup> ) <sub>2</sub> (N <sub>3</sub> ) <sub>8</sub> ] <sub>n</sub>	1.50	2D (e)	-1.9	-14	27
				+27	+54	
<b>8</b>	[Cu <sub>4</sub> (Me-hmpz) <sub>2</sub> (N <sub>3</sub> ) <sub>8</sub> ] <sub>n</sub>	1.00	1D (f)	+41	+102	28
				+28	+55	
<b>9</b>	[Cu <sub>4</sub> (men) <sub>2</sub> (N <sub>3</sub> ) <sub>8</sub> ] <sub>n</sub>	1.00	1D (g)	+58	+112	28
				-14	-59	
<b>10</b>	[Cu <sub>6</sub> (deen) <sub>2</sub> (N <sub>3</sub> ) <sub>12</sub> ] <sub>n</sub>	0.67	3D (h)	+9		24
<b>11</b>	[Cu <sub>6</sub> (aem) <sub>2</sub> (N <sub>3</sub> ) <sub>12</sub> ] <sub>n</sub>	0.67	3D (h)	+11		26
<b>12</b>	[Cu <sub>6</sub> (dmeen) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (N <sub>3</sub> ) <sub>12</sub> ] <sub>n</sub>	1.00	2D (i)	+8		26
<b>13</b>	[Cu <sub>6</sub> (N,N'-dmen) <sub>2</sub> (N <sub>3</sub> ) <sub>12</sub> ] <sub>n</sub>	0.67	2D (j)	+11		26
<b>14</b>	[Cu <sub>6</sub> (hmpz) <sub>2</sub> (N <sub>3</sub> ) <sub>12</sub> ] <sub>n</sub>	0.67	1D (k)	+91		26
<b>15</b>	[Cu <sub>5</sub> (N,N'-dmen) <sub>2</sub> (N <sub>3</sub> ) <sub>10</sub> ] <sub>n</sub>	0.80	2D (l)	-495	-868	28
				+89	+81	
<b>16</b>	[Cu <sub>9</sub> (L <sup>5</sup> ) <sub>4</sub> (N <sub>3</sub> ) <sub>18</sub> ] <sub>n</sub>	1.33	1D (m)			27

<sup>a</sup>The symbols in the brackets have been used to differentiate the types of bridging networks. <sup>b</sup>Only the DFT results of using LanL2DZ basis set are given; for further details, check the references.

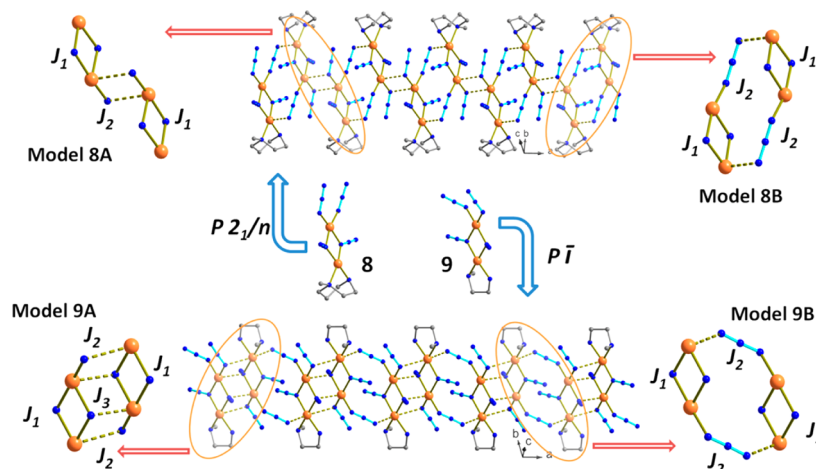
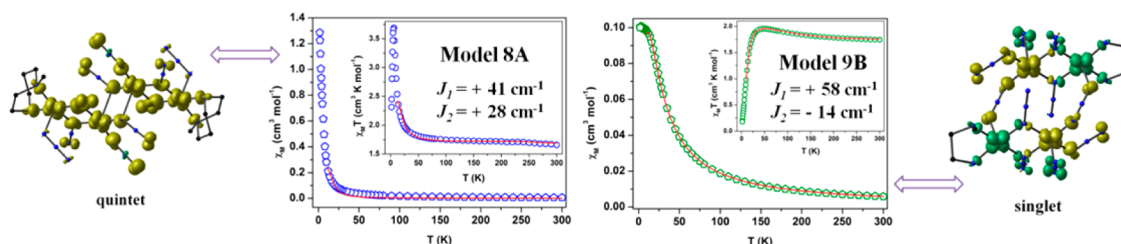


FIGURE 6. Asymmetric unit and 1D structures of complexes **8** and **9**, with different magnetic exchange models.

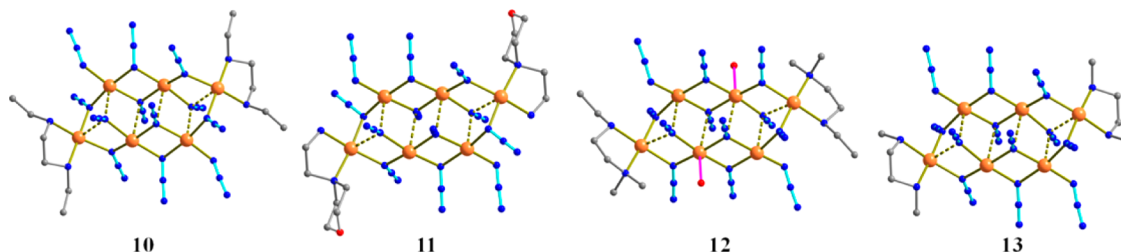
atoms involves a very long bond (weakening the exchange interaction). Both of these bridging azides (an EE-azido group and an EO-azido group with a very high bridging angle) are expected to exchange antiferromagnetically. In **7**, the bond parameters suggest that the bridging between the central pair of metal atoms is very much similar to that of other three complexes (**4–6**). The peripheral Cu atoms are however bridged by double (asymmetric) EO azido groups, with the two Cu–N<sub>EO</sub>–Cu bridging angles on both sides of the cutoff angle (108.6 and 93.6°). The bridging bonds involving the larger angle are smaller (equatorial/apical) than the bonds

(axial/basal) involving the shorter angle. Thus, the small negative value of  $J_1$  can be justified by the competition between a stronger antiferromagnetic interaction and a weaker ferromagnetic interaction.

Using the bidentate ligands 1-methylhomopiperazine (Me-hmpz) and *N*-methylethylenediamine (men), we isolated two more complexes, [Cu<sub>4</sub>(Me-hmpz)<sub>2</sub>(N<sub>3</sub>)<sub>8</sub>]<sub>n</sub> (**8**) and [Cu<sub>4</sub>(men)<sub>2</sub>(N<sub>3</sub>)<sub>8</sub>]<sub>n</sub> (**9**), having the same metal to ligand ratio. The structural similarity of the asymmetric units of the two complexes is remarkable, but the way they build the overall networks is much more interesting. Unlike cases of complexes **4–7**, the



**FIGURE 7.** Plots of  $\chi_M$  and  $\chi_M T$  versus  $T$  for complexes **8** and **9** in the temperature range of 2–300 K. Red lines indicate the fitting. The spin density maps of the calculated spin ground states (quintet for model **8A**; singlet for model **9B**) for the models used.



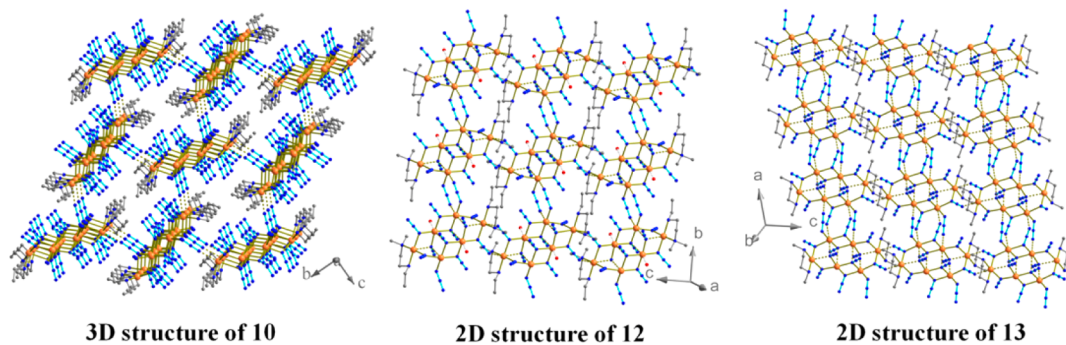
**FIGURE 8.** Basic building units of **10–13**.

asymmetric units of these two complexes join in a sideways fashion. For **9**, they form incomplete double cubanelike secondary structures, which are in turn linked by end-to-end azido bridges. However, for **8**, due to the steric bulk of the ligand, the adjoining asymmetric units cannot come close enough to form cubanelike structures. Both the complexes can be viewed as 1D assemblies of at least two different tetranuclear building units, which are important for explaining the magnetic exchanges by using them as the models for the overall complexes (Figure 6). However, we were only able to fit the data for the linear model (model **8A**) for complex **8** and the noncubane model (model **9B**) for complex **9**. Complex **8** is predominantly ferromagnetic, and the DFT calculations showed that the ground spin state is the quintet state, while the complex **9** has both ferromagnetic and antiferromagnetic exchanges working within the model structural unit, and accordingly it has the singlet state as the ground spin state. Saha et al. and Gu et al. have reported three complexes with ethylenediamine, *N*-propylethylenediamine, and *N*-butylethylenediamine with almost identical structures to that of **9**.<sup>35,36</sup> The complex reported by Saha et al.,  $[\text{Cu}_4(\text{en})_2(\text{N}_3)_8]_n$ , was found to be predominantly antiferromagnetic, and the data could be fitted to the magnetic exchange model **9A** (with all of the exchanges having negative signs).<sup>35</sup> The two complexes reported by Gu et al. were also fitted using this model. Both of the complexes showed two positive and one negative exchange within the cluster system. It is interesting that the overall magnetic behavior (temperature dependence) of complex **9** is similar to that of these last two complexes, but we had to use a different model

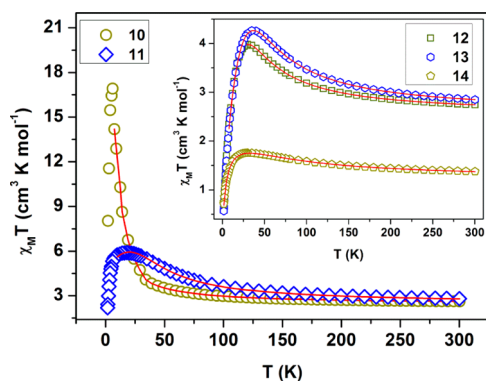
(**9B**) to reasonably fit the magnetic data (Figure 7).<sup>36</sup> At this stage, there seems to be no theoretical justification for choosing a model over the other. However, we should also keep in mind that any cluster exchange model would be inefficient to reproduce the overall magnetic behavior of an extended complex.

### Cu<sub>6</sub> Building Units

In another set of interesting complexes, when the bidentate blocking donor to copper ratio was controlled to 1:3, we found that they all have hexanuclear building units. Among them, four isolated complexes,  $[\text{Cu}_6(\text{deen})_2(\text{N}_3)_{12}]_n$  (**10**),<sup>24</sup>  $[\text{Cu}_6(\text{aem})_2(\text{N}_3)_{12}]_n$  (**11**),  $[\text{Cu}_6(\text{dmeen})_2(\text{N}_3)_{12}(\text{H}_2\text{O})_2]_n$  (**12**), and  $[\text{Cu}_6(\text{N,N'-dmen})_2(\text{N}_3)_{12}]_n$  (**13**)<sup>26</sup> [deen = *N,N'*-diethylethylenediamine, aem = 4-(2-aminoethyl)morpholine, dmeen = *N,N'*-dimethyl-*N'*-ethylethylenediamine, *N,N'*-dmen = *N,N'*-dimethylethylenediamine], have almost identical Cu<sub>6</sub> building units (Figure 8), but two of them (**10** and **11**) grow in three dimensions and the other two (**12** and **13**) grow in only two dimensions. The three-dimensional structure is rather common, as this kind of connectivity is also present in the complexes  $[\text{Cu}_6(\text{N-Eten})_2(\text{N}_3)_{12}]_n$ <sup>30</sup> and  $[\text{Cu}_6(\text{N-Ipren})_2(\text{N}_3)_{12}]_n$ <sup>32</sup> [N-Eten = *N*-ethylethylenediamine, *N*-Ipren = *N*-isopropylethylenediamine] reported by Zuo et al. In these complexes, each Cu<sub>6</sub> unit is joined with two neighboring units through double  $\mu_{1,3}$ -azido bridges parallel to the crystallographic *a* axis and with other four units through a single  $\mu_{1,1,1,3}$ -azido ligand parallel to the *bc* plane to yield a 3D network (Figure 9). Both complexes **12** and **13** crystallize in the triclinic  $P\bar{1}$  space group, and the hexanuclear



**FIGURE 9.** Extended structures of the complexes **10**, **12**, and **13**.



**FIGURE 10.** Plots of  $\chi_M T$  versus  $T$  for complexes **10–14** in the temperature range of 2–300 K. Red lines indicate the fitting. The fitting model for **14** is the same as that used for complexes **1–3**.

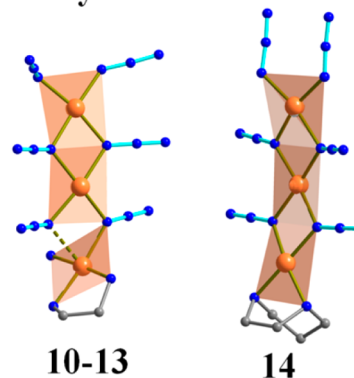
building units form 2D networks. Interestingly, the linking patterns of these two complexes are not similar. It is difficult to rationalize the loss in dimensionality only by the differences in the structures of the diamine ligands. For **12**, however, within the  $\text{Cu}_6$  units, two copper atoms are linked to two coordinating water molecules, which means that these two metal atoms are unavailable to the neighboring unit's azido nitrogen atoms, resulting in a loss of dimensionality to the extended structure. Again, the 2D structure of **13** is probably more surprising as the ligand is not even sterically demanding (compared to the ligands that do give 3D structures), and there are no water molecules in this complex to block coordination sites on the metal atoms.

We assumed that the exchange is uniform through the hexanuclear units and used the following Hamiltonian to derive the required expression for interacting  $\text{Cu}_6$  clusters:

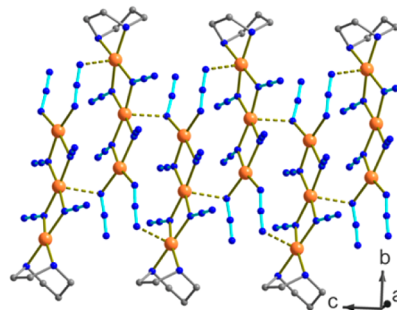
$$H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_5 + S_5S_6 + S_6S_1)$$

All the complexes were found to be predominantly ferromagnetic (Figure 10), and the fitting of the susceptibility data showed that the intracluster interactions range from

### asymmetric units



### 1D structure of 14

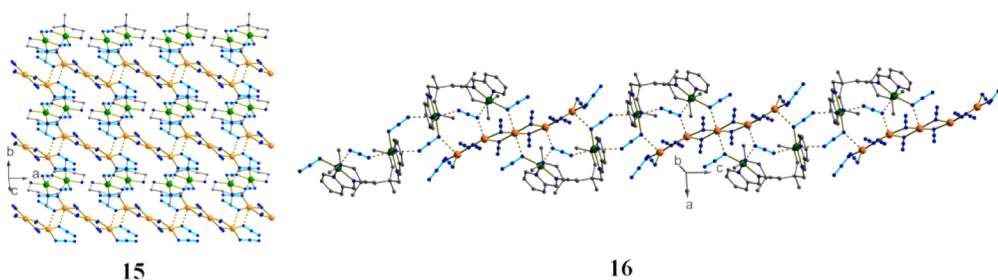


**FIGURE 11.** Differences in the asymmetric unit structures of **10–13** and **14**, and the 1D assembly of **14**.

8 to 12  $\text{cm}^{-1}$ , while the intercluster interactions are negative (with larger magnitudes for the 2D complexes). Interestingly the two similar complexes reported by Zuo and co-workers were found to have positive intercluster exchanges, resulting in a 3D magnetic ordering at lower temperatures.<sup>30,32</sup>

We isolated another such complex using homopiperazine,  $[\text{Cu}_6(\text{hmpz})_2(\text{N}_3)_{12}]_n$  (**14**), which like all the above complexes has a linear trinuclear crystallographic asymmetric unit in which the adjacent copper atoms are linked by double end-on azido bridges. The difference with the other complexes is in the linking of these asymmetric units.





**FIGURE 12.** Extended structures of **15** and **16**. The Cu atoms in the different building units are shown in green and orange.

A closer look at the distribution of the short equatorial bonds in **10–13** of the metal atoms shows that the peripheral copper atom bound to the diamine ligand links to its neighbor within the trinuclear unit in an axial–equatorial manner through one of the end-on azido bridges, while in **14** the equatorial bonds in the asymmetric units are all in almost the same plane (Figure 11). For **14**, there are dimethylene and trimethylene groups situated above and below the chelating plane (consisting of the two N atoms of hmpz and the Cu atom) of the diamine. The steric effects of these alkyl groups may limit the end-on azido bridges close to the chelating plane and may inhibit the close stacking of the trinuclear units necessary to form the basic units of **10–13** and thus a very different (1D) structure emerges.

### Complexes with More than One Building Unit

When a mixture of  $\text{Cu}(\text{NO}_3) \cdot 3\text{H}_2\text{O}$  and excess  $\text{NaN}_3$  was treated with half equivalent (to Cu) of *N,N*-dimethylethylenediamine (*N,N*-dmen), we expected to form a complex resembling **8** or **9**. But surprisingly we isolated the complex with the formula  $[\text{Cu}_5(\text{N,N-dmen})_2(\text{N}_3)_{10}]_n$  (**15**). Structurally, this 2D complex can be viewed as an assembly of centrosymmetric building units  $[\text{Cu}_2(\text{N,N-dmen})_2(\mu_{1,3}\text{-N}_3)_2]^{2+}$  and  $[\text{Cu}_3(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_4]^{2-}$  (Figure 12).

We also isolated a similar complex,  $[\text{Cu}_9(\text{L}^5)_4(\text{N}_3)_{18}]_n$  (**16**), using the Schiff base ( $\text{L}^5$ ) generated in situ from the condensation of pyridine-2-carboxaldehyde and *N,N*-2,2-tetramethylpropanediamine. This complex can be again structurally described as the 1D assembly of the two centrosymmetric building units  $[\text{Cu}_4(\text{L}^5)_4(\mu_{1,3}\text{-N}_3)_4]^{2+}$  and  $[\text{Cu}_5(\mu_{1,1}\text{-N}_3)_8(\text{N}_3)_4]^{2-}$  (Figure 12). In the cationic unit, the central Cu atoms are joined by EE-azido bridges only. In the anionic unit, the five copper atoms are linearly joined by four sets of double symmetric (involving only short bonds) EO-azido bridges. The neighboring cationic and anionic units are linked by three end-on azido groups (belonging to the cationic units) and stack alternatively to form the overall one-dimensional structure of the complex.

### Conclusion and Future Perspectives

In this Account, we have only reviewed the possibility of forming new magnetically interesting structures using the concept of opening up coordination sites by decreasing the amount of blocking ligands in copper(II)-azido complexes. Copper(II) is unique among the transition metals, as it can form four to six bonds and is not prejudiced to perfect coordination geometries. In other words, copper(II) provides a degree of “coordinative flexibility” necessary to explore new horizons in structural and magneto-chemistry. The magnetic exchanges of the spin half ( $S = 1/2$ ) metal can also be easily interpreted using its bonding parameters. Therefore, it is only logical, based on the success with this metal, to extend the concept described here to other metal systems. Like copper(II), nickel(II) also forms many azido complexes with diamine or similar blocking ligands.<sup>12</sup> Generally, cobalt(II) gets oxidized to diamagnetic cobalt(III) in the presence of aliphatic amines. This can be prevented by using small amounts of reducing agents that do not interfere with the main process of complex formation, but this method is not always successful. However, if the ligand itself were a reducing agent (e.g., hydrazine,  $\text{N}_2\text{H}_4$ ), we can use it to our advantage. Gao et al. reported a complex of the formula  $[\text{Co}(\text{N}_2\text{H}_4)(\text{N}_3)_2]_n$  with a layered honeycomb structure and showing weak spin-canted antiferromagnetism.<sup>40</sup> We were able to synthesize another complex with lower molar equivalent of hydrazine,  $[\text{Co}_3(\text{N}_2\text{H}_4)_2(\text{N}_3)_6]_n$ , which was found to be a 3D complex and showed interesting low temperature magnetic ordering.<sup>41</sup> For the Co-azido systems, monodentate pyridine based ligands have been successfully used to synthesize complexes with different ratios of metal to ligand.<sup>42,43</sup>

Crystallization of extended molecular complexes is still not well understood. Therefore, our concept of using the same components to form a number of complexes by ratio variation would help molecular engineers to develop new structures with tunable properties, even though the synthesis is still largely serendipitous. The concept developed by

our group and some others discussed here does not necessarily have to be confined to metal-azido systems and thus the opportunities in this field of study have been increased many folds for the development of new polyclusters with exciting magnetic properties. We hope that through these random examples, a database can be developed and with a huge number of such complexes, a better understanding of the 'Serendipitous Assemblies' will eventually arise. Our group is in active search for extending this concept to metal ions having more than one unpaired electrons for the generation of polyclusters with exciting magnetic behavior.

*We gratefully acknowledge the contributions of co-workers and colleagues whose names are listed as coauthors in the papers we have cited from our group. We also thank the Department of Science and Technology (DST), India, for the financial support.*

#### BIOGRAPHICAL INFORMATION

**Sandip Mukherjee** was born in West Bengal, India, in 1984. He received his B.Sc. in chemistry in 2005 from the University of Calcutta and M.Sc. in chemistry in 2007 from IIT- Madras. Since 2007, he has been working with Prof. P. S. Mukherjee in the Indian Institute of Science for Ph.D. His principal research interest concerns various aspects of molecular magnetism and application of density functional theory in molecular magnetism.

**Partha Sarathi Mukherjee** received his Ph.D. in 2002 working with Prof. N. Ray Chaudhuri at Indian Association for the Cultivation of Science, and his postdoctoral from University of Utah with Prof. Peter J. Stang. In 2004, he moved to University of Goettingen to work with Prof. Herbert W. Roesky as a Humboldt fellow. He has been at the Indian Institute of Science, Bangalore, since July 2005, where he is currently an Associate Professor. His current research interests are in the areas of self-assembly of functional molecular architectures and magnetic polyclusters. He is the recipient of a young scientist medal of the Indian National Science Academy, Associate-ship of the Indian Academy of Sciences, Young Affiliate Fellowship of the Third World Academy of Sciences (Trieste), Swarnajayanti Fellowship of Govt. of India, SCOPUS young scientist award by Elsevier, and Microsoft Research outstanding young faculty award. Dr. Mukherjee has published 103 original papers in peer-reviewed journals.

#### FOOTNOTES

\*To whom correspondence should be addressed. Fax: 91-80-23601552. Tel: 91-80-22933352. E-mail: psm@ipc.iisc.ernet.in.  
The authors declare no competing financial interest.

#### REFERENCES

- Zhao, D.; Timmons, D. J.; Yuan, D.; Zhou, H.-C. Tuning the Topology and Functionality of Metal-Organic Frameworks by Ligand Design. *Acc. Chem. Res.* **2011**, *44*, 123–133.
- Farha, O. K.; Hupp, J. T. Rational Design, Synthesis, Purification, and Activation of Metal-Organic Framework Materials. *Acc. Chem. Res.* **2010**, *43*, 1166–1175.
- Ockwig, N. W.; Delgado-Friedrichs, O.; O'keeffe, M.; Yaghi, O. M. Reticular Chemistry: Occurrence and Taxonomy of Nets and Grammar for the Design of Frameworks. *Acc. Chem. Res.* **2005**, *38*, 176–182.

- Leong, W. L.; Vittal, J. J. One-Dimensional Coordination Polymers: Complexity and Diversity in Structures, Properties, and Applications. *Chem. Rev.* **2010**, *111*, 688–764.
- Li, J.-R.; Sculley, J.; Zhou, H.-C. Metal Organic Frameworks for Separations. *Chem. Rev.* **2012**, *112*, 869–932.
- Cui, Y.; Yue, Y.; Qian, G.; Chen, B. Luminescent Functional Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 1126–1162.
- Xuan, W.; Zhu, C.; Liu, Y.; Cui, Y. Mesoporous metal–organic framework materials. *Chem. Soc. Rev.* **2012**, *41*, 1677–1695.
- Kostakis, G. E.; Perlepes, S. P.; Blatov, V. A.; Proserpio, D. M.; Powell, A. K. High nuclearity cobalt coordination clusters: Synthetic, topological and magnetic aspects. *Coord. Chem. Rev.* **2012**, *256*, 1246–1278.
- Murrie, M. Cobalt(II) single-molecule magnets. *Chem. Soc. Rev.* **2010**, *39*, 1986–1995.
- Kostakis, G. E.; Akoa, A. M.; Powell, A. K. Structural motifs and topological representation of Mn coordination clusters. *Chem. Soc. Rev.* **2010**, *39*, 2238–2271.
- Wang, X.-Y.; Wang, Z.-M.; Gao, S. Constructing magnetic molecular solids by employing three-atom ligands as bridges. *Chem. Commun.* **2008**, 281–294.
- Ribas, J.; Escuer, A.; Monfort, Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. Polynuclear Ni<sup>II</sup> and Mn<sup>II</sup> azido bridging complexes. Structural trends and magnetic behaviour. *Coord. Chem. Rev.* **1999**, *193–195*, 1027–1068.
- Adhikari, C.; Koner, S. Structural and magnetic studies on copper(II) azido complexes. *Coord. Chem. Rev.* **2010**, *254*, 2933–2958.
- Zeng, Y.-F.; Hu, X.; Liu, F.-C.; Bu, X.-H. Azido-mediated systems showing different magnetic behaviours. *Chem. Soc. Rev.* **2009**, *38*, 469–480.
- Boudalis, A. K.; Donnadiou, B.; Nastopoulos, V.; Clemente-Juan, J. M.; Mari, A.; Sanakis, Y.; Tuchagues, J.-P.; Perlepes, S. P. A Nonanuclear Iron(II) Single-Molecule Magnet. *Angew. Chem., Int. Ed.* **2004**, *43*, 2266–2270.
- Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. Magnetic Coupling in End-On Azido Bridged Transition Metal Complexes: A Density Functional Study. *J. Am. Chem. Soc.* **1998**, *120*, 11122–11129.
- Maji, T. K.; Mukherjee, P. S.; Mostafa, G.; Mallah, T.; Cano-Boquera, J.; Chaudhuri, N. R. First observation of a ferromagnetic interaction through an end-to-end azido bridging pathway in a 1D copper(II) system. *Chem. Commun.* **2001**, 1012–1013.
- Mukherjee, P. S.; Dalai, S.; Zangrando, E.; Lloret, F.; Chaudhuri, N. R. The first metamagnetic one-dimensional molecular material with nickel(II) and end-to-end azido bridges. *Chem. Commun.* **2001**, 1444–1445.
- Ribas, J.; Monfort, M.; Ghosh, B. K.; Solans, X. The Versatility of the Azido Ligand: Linkage of Ni<sup>II</sup> Centers to Form a Chain with One End-to-End and Three End-On Bridges in Alternation. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2087–2089.
- Naiya, S.; Biswas, C.; Drew, M. G. B.; Gomez-Garcia, C. J.; Clemente-Juan, J. M.; Ghosh, A. A Unique Example of Structural and Magnetic Diversity in Four Interconvertible Copper(II)–Azide Complexes with the Same Schiff Base Ligand: A Monomer, a Dimer, a Chain, and a Layer. *Inorg. Chem.* **2010**, *49*, 6616–6627.
- Saha, S.; Koner, S.; Tuchagues, J.-P.; Boudalis, A. K.; Okamoto, K.-I.; Banerjee, S.; Mal, D. Cation-Dependent Nuclearity of the Copper-Azido Moiety: Synthesis, Structure, and Magnetic Study. *Inorg. Chem.* **2005**, *44*, 6379–6385.
- Goher, M. A. S.; Cano, J.; Jourmaux, Y.; Abu-Youssef, M. A. M.; Mautner, F. A.; Escuer, A.; Vicente, R. Synthesis, Structural Characterisation, and Monte Carlo Simulation of the Magnetic Properties of the 3D-Stacked Honeycomb Cs<sub>2</sub>[(Mn(N<sub>3</sub>)<sub>3</sub>)<sub>n</sub>] and the Irregular Double Chain [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>n</sub>[(Mn<sub>2</sub>(N<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O))<sub>n</sub>]. *Chem.—Eur. J.* **2000**, *6*, 778–784.
- Mondal, K. C.; Mukherjee, P. S. Three New Cu-Azido Polymers and Their Systematic Interconversion: Role of the Amount of the Blocking Amine on the Structural Diversity and Magnetic Behavior. *Inorg. Chem.* **2008**, *47*, 4215–4225.
- Mukherjee, S.; Gole, B.; Chakrabarty, R.; Mukherjee, P. S. Cu<sup>II</sup>-Azide Polymers of Cu<sub>3</sub> and Cu<sub>6</sub> Building Units: Synthesis, Structures, and Magnetic Exchange Mechanism. *Inorg. Chem.* **2009**, *48*, 11325–11334.
- Sengupta, O.; Gole, B.; Mukherjee, S.; Mukherjee, P. S. A series of transition metal azido extended complexes with various anionic and neutral co-ligands: synthesis, structure and their distinct magnetic behaviour. *Dalton Trans.* **2010**, *39*, 7451–7465.
- Mukherjee, S.; Mukherjee, P. S. A Series of Cu<sup>II</sup>-Azide Polymers of Cu<sub>6</sub> Building Units and the Role of Chelating Diamine in Controlling their Dimensionality: Synthesis, Structures, and Magnetic Behavior. *Inorg. Chem.* **2010**, *49*, 10658–10667.
- Mukherjee, S.; Gole, B.; Song, Y.; Mukherjee, P. S. Synthesis, Structures, and Magnetic Behavior of a Series of Copper(II) Azide Polymers of Cu<sub>4</sub> Building Clusters and Isolation of a New Hemiaminal Ether as the Metal Complex. *Inorg. Chem.* **2011**, *50*, 3621–3631.
- Mukherjee, S.; Patil, Y. P.; Mukherjee, P. S. Cu<sup>II</sup>-azide polymers with various molar equivalents of blocking diamine ligands: synthesis, structures, magnetic properties with DFT studies. *Dalton Trans.* **2012**, *41*, 54–64.
- Mukherjee, S.; Mukherjee, P. S. Cu<sup>II</sup>-azide polynuclear complexes of Cu<sub>4</sub> building clusters with Schiff-base co-ligands: synthesis, structures, magnetic behavior and DFT studies. *Dalton Trans.* **2013**, *42*, 4019–4030.

- 30 Gu, Z.-G.; Zuo, J.-L.; You, X.-Z. A three-dimensional ferromagnet based on linked copper–azido clusters. *Dalton Trans.* **2007**, 4067–4072.
- 31 Abu-Youssef, M. A. M.; Escuer, A.; Mautner, F. A.; Ahrstrom, L. An unusual 3D-topology and dominant ferromagnetic couplings in two Cu(II)–azide coordination polymers. *Dalton Trans.* **2008**, 3553–3558.
- 32 Gu, Z.-G.; Xu, Y.-F.; Yin, X.-J.; Zhou, X.-H.; Zuo, J.-L.; You, X.-Z. Cluster-based copper(II) coordination polymers with azido bridges and chiral magnets. *Dalton Trans.* **2008**, 5593–5602.
- 33 Jia, Q.-X.; Bonnet, M.-L.; Gao, E.-Q.; Robert, V. Competing Large and Small Angles in a Double End-On Azido Copper(II) Binuclear Complex: A Combined Experimental and Theoretical Study of Magnetic Interactions. *Eur. J. Inorg. Chem.* **2009**, 3008–3015.
- 34 Tian, C.-B.; Li, Z.-H.; Lin, J.-D.; Wu, S.-T.; Du, S.-W.; Lin, P. Cluster-Based Cu<sup>II</sup>–Azide Polymers: Synthesis, Structure, Magnetic Properties, and Effect of Polyamines on Crystal Structures. *Eur. J. Inorg. Chem.* **2010**, 427–437.
- 35 Saha, S.; Biswas, D.; Chakrabarty, P. P.; Jana, A. D.; Boudalis, A. K.; Seth, S. K.; Kar, T. Cluster based copper(II)-azide polymer: Synthesis, structure and magnetic study. *Polyhedron* **2010**, *29*, 3342–3348.
- 36 Gu, Z.-G.; Na, J.-J.; Wang, B.-X.; Xiao, H.-P.; Li, Z. Novel copper–azido magnetic molecular tapes: syntheses, structures, and magnetic properties. *CrystEngComm* **2011**, *13*, 6415–6421.
- 37 Stamatatos, T. C.; Papaefstathiou, G. S.; MacGillivray, L. R.; Escuer, A.; Vicente, R.; Ruiz, E.; Perlepes, S. P. Ferromagnetic Coupling in a 1D Coordination Polymer Containing a Symmetric [Cu( $\mu_{1,1}$ -N<sub>3</sub>)<sub>2</sub>Cu( $\mu_{1,1}$ -N<sub>3</sub>)<sub>2</sub>Cu]<sup>2+</sup> Core and Based on an Organic Ligand Obtained from the Solid State. *Inorg. Chem.* **2007**, *46*, 8843–8850.
- 38 Luo, J.; Zhou, X.-G.; Gao, S.; Weng, L.-H.; Shao, Z.-H.; Zhang, C.-M.; Li, Y.-R.; Zhang, J.; Cai, R.-F. Synthesis and characterization of copper(II) azide complexes containing polyamines as co-ligands. *Polyhedron* **2004**, *23*, 1243–1248.
- 39 Song, Y.; Massera, C.; Quesada, M.; Lanfredi, A. M. M.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. A one-dimensional copper(II) coordination polymer [Cu<sub>3</sub>(ampym)<sub>2</sub>( $\mu_{1,1}$ -N<sub>3</sub>)<sub>4</sub>( $\mu_{1,3}$ -N<sub>3</sub>)<sub>2</sub>(dmf)<sub>2</sub>]<sub>n</sub> (ampym = 2-aminopyrimidine) containing both end-on and end-to-end azido bridges. *Inorg. Chim. Acta* **2005**, *358*, 1171–1178.
- 40 Wang, X.-T.; Wang, Z.-M.; Gao, S. Honeycomb Layer of Cobalt(II) Azide Hydrazine Showing Weak Ferromagnetism. *Inorg. Chem.* **2007**, *46*, 10452–10454.
- 41 Sengupta, O.; Mukherjee, P. S. Three-component assembly of a metal–inorganic 3D Co(II) polymer containing bridging hydrazine. *Dalton Trans.* **2009**, *38*, 7599–7601.
- 42 Abu-Youssef, M. A. M.; Mautner, F. A.; Vicente, R. 1D and 2D End-to-End Bridged Cobalt(II) Complexes: Syntheses, Crystal Structures, and Magnetic Properties. *Inorg. Chem.* **2007**, *46*, 4654–4659.
- 43 Escuer, A.; Mautner, F. A.; Sodin, B.; Goher, M. A. S.; Vicente, R. Topologic ferrimagnetism in cobalt(II)-azido chains. *Dalton Trans.* **2010**, *39*, 4482–4484.