International Journal of Engineering, Science and Mathematics
Vol. 7, Special Issue 4(1), April 2018,
ISSN: 2320-0294 Impact Factor: 6.765
Journal Homepage: http://www.ijmra.us, Email: editorijmie@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

Structural And Magnetic Properties of Some Dinuclear End On Azido Bridged Copper(II) Complexes

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Abstract

In this review some single and doubly end-on azido bridged dinulear complexes and their magnetic behavior was described. The magnetic properties of the complexes depends on the Cu- N_3-Cu angle, Cu-Cu separation, geometry around the metal centres, Cu-N_3 bond distance and also on nature of the coligand. If azide ion binds two metal centres in basal-basal fashion then it has been proposed that the accidental orthogonality in the *end-on* azide bridge occurs at Cu–N_3–Cu bond angles close to 104° (theory) or 108° (experiment), then for very large Cu–N_3(EO)–Cu bond angles (>108°), the magnetic coupling should be antiferromagnetic.

Keywords:

Copper;
Azide;
Dinuclear;
End on bridge.

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1. Introduction

A variety of synthetic strategies have been applied to build multinuclear molecular architectures with different terminal and bridging ligands to facilitate ferro- and antiferromagnetic interactions among the metal centres [1-4]. Amongst the metal-based systems, several families such as oxalato ($C_2O_4^{2-}$) [5,6], cyano (CN^-) [6–8], oximato[9], azido (N_3^-) [10] and dicyanomido($N(CN)_2^-$) [11] bridged compounds play important roles in the understanding of basics of molecular magnetism. As bridging ligands, pseudohalides are good choice, due to their versatile coordination behavior that generates di- [12,13] and polynuclear magnetic materials [14-17]. Amongst them azido ligand has been extensively used as it affords an efficient super exchange pathway between paramagnetic centers such as Cu(II), Ni(II), Mn(II), Mn(III), Fe(III), etc. [18-24].

As bridging bidentate ligand azide binds the metal via end-on(EO) (Fig. 1b–c) and end-to-end (EE) (Fig. 1d–e) mode. The EO coordination modes are of two types: (i)$\mu_{1,1}$-N_3 (namely single EO) (Fig. 1b) and (ii) di-$\mu_{1,1}$-N_3(double EO) (Fig. 1c). The EE coordination modes are also of two types: (i)$\mu_{1,3}$-N_3(single EE) (Fig. 1d) and (ii) di- $\mu_{1,3}$-N_3(double end-to-end) (Fig. 1e). The possible tridentate bridging coordination modes of azido ligand are $\mu_{1,1,1}$-N_3(Fig. 1f) and $\mu_{1,1,3}$-N_3(Fig. 1g), respectively [25]. A rare variety of coordination mode $\mu_{1,1,1,1}$-N_3 (Fig. 1h) was observed in a few nickel(II) and cobalt(II) complexes [25,26]. An, unprecedented azido coordination modes like $\mu_{1,1,3,3}$-N_3(Fig. 1i) and $\mu_{1,1,1,3,3,3}$-N_3(Fig. 1j) have been reported [22].

The different coordination modes of the azide bridging result a wide range of magnetic behaviors. Generally, the complexes with the end-on (EO) mode exhibit ferromagnetic coupling (F-interaction) [27,28], whereas with the end-to-end (EE) mode show antiferromagnetic (AF interaction) behavior through the very effective superexchange pathway of azide anion. The type and the magnitude of the magnetic exchange interaction depends on the bridge identity, the metal–metal separation, the bond angles subtended to the bridging atoms, the dihedral angles between the planes containing the metal ions, the metal bridging ligand bond lengths, and the metal ion stereo-chemistries. Furthermore, various factors such as strict and accidental

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orthogonality of magnetic orbitals, spin polarization, and delocalization of un-paired electrons including charge transfer, have considerable influence in determining the nature of the magnetic coupling between spin centers [29]. The first approach for calculation was undertaken by means of extended Hückel method [5]. However it has been proposed that the accidental orthogonality in the end-on azide bridge occurs at Cu–N_3–Cu bond angles close to 104° (theory) or 108° (experiment), for very large Cu–N_3(EO)–Cu bond angles (>108°), the magnetic coupling should be antiferromagnetic [3,4]. Therefore, the magnetic properties of the end-on azide bridged compounds depend on the Cu–N_3(EO)–Cu bond angles [3,4]. Considering the magnetic interactions, the topology regarding the planarity of the two magnetic orbitals with the bridging plane is the key factor influencing the exchange interaction. The ferromagnetic interaction between the transition metal ions is one of the interesting topologies. Complexes with asymmetric end-on azido bridge are rare and the interaction between metal centers is weak to moderately strongly ferromagnetic [30].

The theoretical study of the magnetic behavior of binuclear transition metal complexes represents a great challenge due to the existence of a manifold of states separated by small energy differences. A qualitative approach that has been employed successfully for the interpretation of magneto-structural correlations is that proposed by Hay, Thibeault, and Hoffmann [31]. From Hartree-Fock theory, they deduced an approximate formula for the exchange coupling constant *J* associated to the energy separation between states of different spin multiplicity which, for the case of two centers with one unpaired electron each, can be given by

$$J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)}{J_a - J_b} (1)$$

In eq 1, ε_1 and ε_2 are the energies of the molecular orbitals associated with the unpaired electrons (SOMO's), while *K*ab, *J*aa, and *J*ab are two-electron integrals. The positive term in eq 1 represents a ferromagnetic contribution and the second terman antiferromagnetic contribution, so the nature of the exchange coupling will be ferro- or antiferromagnetic depending on the relative weight of the two terms. The main application of eq 1 so far consists of assuming that the two-electron terms areapproximately constant for compounds with the same metal atoms and bridging ligand, which leads to a direct relationship between the coupling constant *J* and the energy gap between the two SOMO's. The limitations of such model, is that one cannot account for differences between strongly ferromagnetic systems (i.e., when the last term in eq 1 is close to zero). The advantage of such approximation is that the variations of the orbital gap with changes in structural parameters can be reasonably estimated through semiempirical calculations. But more precise theoretical estimates of the exchange coupling constant can be obtained using ab initio methods [32-35]. Ruiz et. al. have explored a third way, consisting in the use of hybrid density functional methods (DFT) [36] combined with the broken-symmetry approach proposed by Noodlemann [37] which has been successfully applied to the study of the magnetic properties of hydroxo-, alkoxo-[38] and oxalato-bridged [39] Cu-(II) binuclear complexes [40].

In experimental study to calculate the J value of dimeric structure of the complex, the $\chi_M T$ curve has been fitted using a classical Bleaney and Bowers law, using the phenomenological Hamiltonian H= $-JS_A.S_B$ [5]. The resulting law used for fitting has the following form:

$$\chi_M T = \frac{2Ng^2\beta^2}{k\left[3 + \exp\left(-J/kT\right)\right]}$$

It has been observed that the longer the bond distances of M–N_3(EO), the weaker the F interactions will be. The exchange coupling switches into AF interaction at Cu–N distances larger than 2.05 Å for a Cu(II) system. The geometry of the Cu(II) centres are obtained from the τ value, [$\tau = \beta-\alpha/60^{\circ}$; where β and α are the two largest angles around the central atom]; τ = 0 and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively [41]. Magnetic interaction will also depend on the corresponding τ value of the complex. Although the out of plane displacement of an EO azido group has a small effect on exchange coupling from theoretical calculations, experimental data suggest that a good coplanar structure ($\Delta_{1,1}$ close to 0◦) leads to strong F coupling (J increases). The AF coupling becomes small as the dihedral angle $\Delta_{1,3}$ increases for double EE azido bridging complexes. That is, the coplanarity would enhance AF interactions (−J increases). The longer the distance of M–N_3(EE), the poorer is the AF coupling. A larger M...M distance would weaken the exchange interaction. The M–N–N angle and dihedral M–NNN–M angle $\Delta_{1,3}$ are the two main factors to affect the nature of coupling J in a single EE azido system.

A review on the structural and magnetic studies on copper(II) azido complexes was reported by Adhikary and Koner in 2010 [29], in this review I only focussed on the structure and magnetic properties of some single and double end-on azido bridged dinuclear copper(II) complexes.

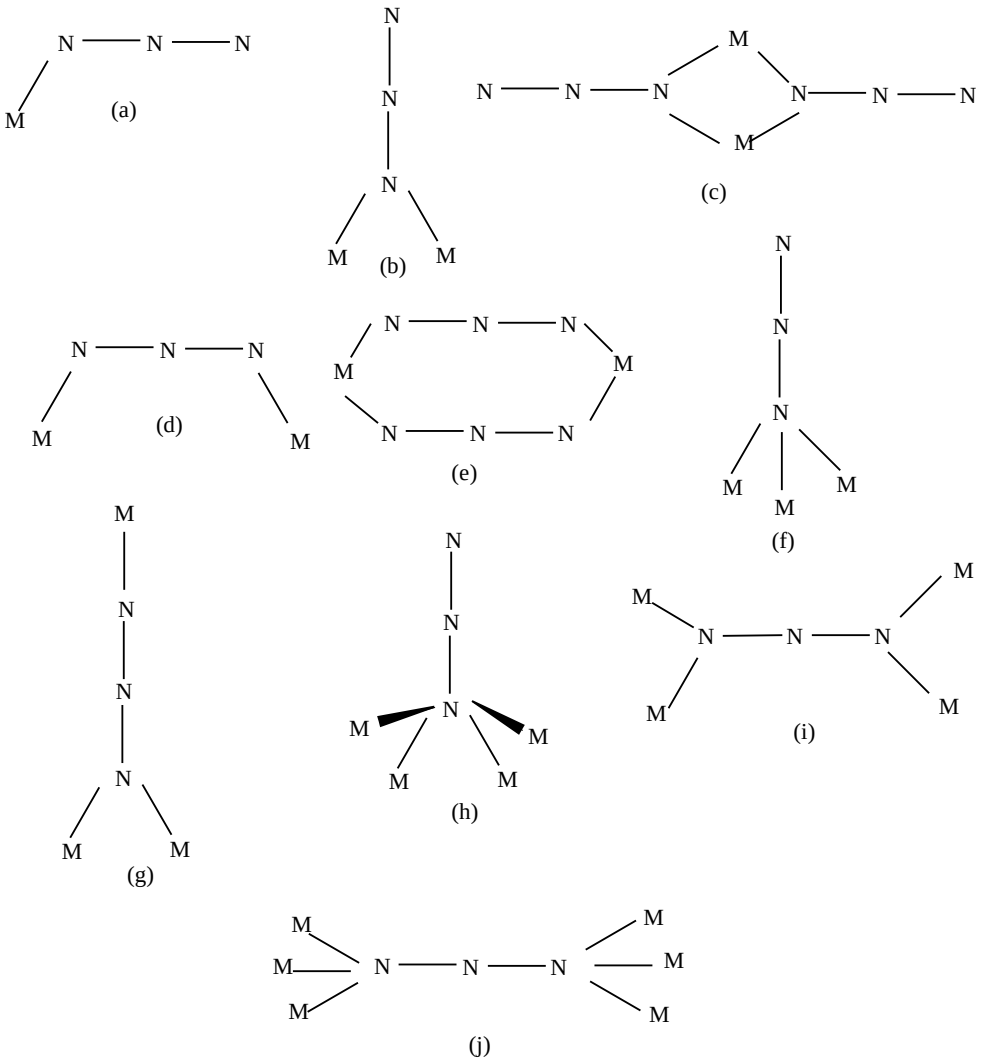


Fig. 1. Different binding modes of azide (N_3^-) ion

2. Azide bridged dinuclear copper complexes

Azide ion can bind the two copper ions in single or double end on bridging mode. End on azido bridging coordination modes are two types: (i) symmetric end on azido bridges and (ii) asymmetric end on azido bridges. For symmetric binding mode azide nitrogen atoms bind the two metal centres in basal-basal fashion. On the other hand for asymmetric binding mode the azide nitrogen atoms binds the two metal centres in basal-apical fashion.

2.1. Single end-on azide bridged copper complexes

The magnetic and structural data of some asymmetric single end on azide bridged dinuclear copper(II) complexes are given in Table 1. In the first dinuclear copper (II) complex $[Cu_2(\mu\text{-}N_3)(\mu\text{-}Lm)_2](ClO_4)_3$ (**1**) (Lm=bis[bis(1-pyrazolyl)methyl]benzene) [42] the azide adopts end-on ($\mu\text{-}_{1,1}$) coordination with a Cu−N−Cu angle of 138.0° and the copper atoms adopts distorted square pyramidal geometry. Complex show usual antiferromagnetic interaction with J = -223 cm^{-1}as expected for Cu-N-Cu angle greater than 108 ° and DFT calculations indicate a predominantly dx^2-y^2 is the ground state for the complex. Conversely the second complex $[Cu_2(dmterpy)_2(\mu\text{-}_{1,1}\text{-}N_3)(N_3)_2]$ .NO_3. $(H_2O)_2$ (**2**) [dmterpy = 5,5"dimethyl-2,2' :6' ,2"-terpyridine] shows weak ferromagnetic interaction with J = 2.88cm^{-1} despite the large *end-on* azide bridge angle (117.4 (2)°) [43] which indicates that as here the Cu(II) ions adopts square pyramidal geometry and the azide ion adopts a basal-epical asymmetric disposition between copper ions so not the bridging angle but other factors like large Cu-Cu separation, and long Cu azide nitrogen bond length and geometry around the copper atoms are the cause for this ferromagnetic interaction. Thompson and his coworkers reported eleven single end on azide bridged dinuclear copper complexes (complex **3** to **13** in Table 1) $[Cu_2(DMPTD)(\mu_2\text{-}N_3)(\mu_2\text{-}Cl)Cl_2].CH_3CN$ **(3),** $[Cu_2(DMPTD)(\mu_2\text{-}N_3)(\mu_2\text{-}Br)Br_2].CH_3CN$ **(4),** $[Cu_2$ $(DIP)(\mu_2\text{-}N_3)(\mu_2Cl)Cl_2]0.5$ CH_3OH

(**5**), [Cu_2 (DIP)(μ_2-N_3)(μ_2Br)Br_2]0.5 CH_3OH (**6**), [Cu_2(PAP)(μ_2-N_3)Cl_3].CH_2Cl_2(**7**), [Cu_2(PAP)(μ_2-N_3)($N0_3$)$_3$)].($CH_3$0H). $N0_3$. $CH_3$0H (**8**), [Cu_2(PPD3Me)(μ_2-N_3)Cl_3].$(H_2O)_{1.5}$(**9**), [Cu_2(PPD3Me)(μ_2-N_3)Br_3].0.5CH_3CN **(10)**, [Cu_2(PPD3Me)(μ_2-N_3)(NO_3)$_3$].0.5CH_3CN (**11**), [Cu_2(PPD)(μ_2-N_3)(NO_3)$_3$$(H_2O)_{1.6}$] **(12),** [$Cu_2$ (PAP46MeH)(μ_2-N_3)(N_3)2]0.33H_2O9 (**13**) (where DMPTD = 2,5-bis((pyridylmethy1)thio) thiadiazole, DIP = 3,6-bis(2'- imidazolyl- 1'-methyl)thio)pyridazine, PAP46Me = 1,4-bis((4',6'-dimethyl-2'-pyridyl)amino)phthalazine [44]. Amongst them the first four complexes show moderate to strong ferromagnetic interaction like **1** which agree with their structural parameters, and also the *spin polarization* is the major reason for the presence of ferromagnetic coupling. The remaining seven complexes show antiferromagnetic interaction and the magnitude of the J values increases with copper azide bridging angles (Table 1). But for complex **13** the value is much less may be due to the delocalization of the negative charge of the ligand PAP46Me.

Table 1. Structural and magnetic parameters for asymmetric single end on (μ-$_{1,1}$-N_3) azido bridged transition metal complexes

Compounds	Cu-Cu(Å)	Cu-N(Å)	Cu-N-Cu(°)	J(cm^{-1})	Ref.
[Cu_2(μ-N_3)(μ-Lm)$_2$](ClO_4)$_3$(**1**)	3.084	2.054	138.0	-223	42
[Cu_2(dmterpy)$_2$(μ-$_{1,1}$-N_3)(N_3)$_2$] . NO_3 . (H_2O)$_2$ (**2**)	3.674	1.991, 20305	117.4	2.88	43
[Cu_2(DMPTD)(μ_2-N_3)(μ_2.Cl)Cl_2].CH_3CN (**3**)	3.1215	1.965, 1.947	105.9	84	44
[Cu_2(DMPTD)(μ_2-N_3)(μ_2.Br)Br_2].CH_3CN (**4**)	-	-	-	59	44
[Cu_2 (DIP)(μ_2-N_3)(μ_2Cl)Cl_2]0.5 CH_3OH (**5**)	-	-	-	78	44
[Cu_2 (DIP)(μ_2-N_3)(μ_2Br)Br_2]0.5 CH_3OH (**6**)	-	-	-	30	44
[Cu_2(PAP)(μ_2-N_3)Cl_3].CH_2Cl_2(**7**)	3.1649	1.968, 1.946	107.9	-20	44
[Cu_2(PAP)(μ_2-N_3)($N0_3$)$_3$)].($CH_3$0H). $N0_3$. $CH_3$0H (**8**)	3.177	1.959, 1.954	108.6	-53	44
[Cu_2(PPD3Me)(μ_2-N_3)Cl_3].$(H_2O)_{1.5}$(**9**)	3.510	1.980, 1.996	124.1	-389	44
[Cu_2(PPD3Me)(μ_2-N_3)Br_3].0.5CH_3CN **(10)**	-	-	-	-546	44
[Cu_2(PPD3Me)(μ_2-N_3)(NO_3)$_3$].0.5CH_3CN (**11**)	-	-	-	-225	44
[Cu_2(PPD)(μ_2-N_3)(NO_3)$_3$$(H_2O)_{1.6}$] (**12**)	3.439	1.988	119.8	-234	44
[Cu_2 (PAP46MeH)(μ_2-N_3)(N_3)2]0.33H_2O9 (**13**)	-	-	-	-97	44

2.2. Double end-on azide bridged copper complexes

The magnetic and structural data of some asymmetric double end on azide bridged dinuclear copper(II) complexes are given in Table 2. From the data of the Table it is found that for the first three asymmetric basal–apical, $\mu_{1,1}$-azide bridged complexes, [$CuL1(N_3)]_2$ (**14**), [$CuL_2(N_3)]_2$ (**15**) and [$CuL_3(N_3)]_2$(**16)** with very similar tridentate Schiff base blocking ligands [L1= *N*-(3-aminopropyl)salicylaldimine, L2= 7-amino-4-methyl-5-azahept-3-en-2-one and L3= 8-amino-4-methyl-5-azaoct-3-en-2-one) have the Cu–N–Cu angles 90.5° , 86.82° and 93.60° respectively [45]. Here the former two complexes have antiferromagnetic coupling with J =-1.84 cm^{-1} for **14** and J= -3.10 cm^{-1} for **15 .**Though the **c**omplex **16** has greater Cu–N–Cu angles than the other two complexes but it exhibits ferromagnetic coupling with J= 0.26 cm^{-1}[30]. Here also it is not possible to explain this different magnetic behavior from only Cu–N–Cu angles because the magnetic pathway is not *basal–basal*. From Table 2 we can see that complex **16** has the largest Cu–Cu distance (3.318 Å), the largest Cu–N–Cu angle {93.60° and the largest τ parameter (0.26) [30]} so the combination of these three features may explain the experimental ferromagnetic character of **16**. A novel Schiff base copper(II) complex [Cu_2(L4)(N_3)$_2$](ClO_4)$_2$], (**17**) {where L4=(4-imidazolyl)ethylene-2-amino-1-ethylpyridine}, containing double end on azide-bridges between adjacent copper ions in a dinuclear arrangement was reported by Alves et. al. [45], where the two copper(II) ions adopt tetragonal pyramidal coordination geometry and antiferromagnetic interaction is operating between the copper centres. Further, in solid state, two different values for magnetic coupling in this species were obtained, J/k =−(5.14 ±0.02) cm^{-1}attributed to the $\mu_{1,1}$azide-bridge mode, and J′z′/k =−(2.94 ±0.11) $cm^{-1}$for the interaction between dinuclear moieties via water/perchorate bridges [45].

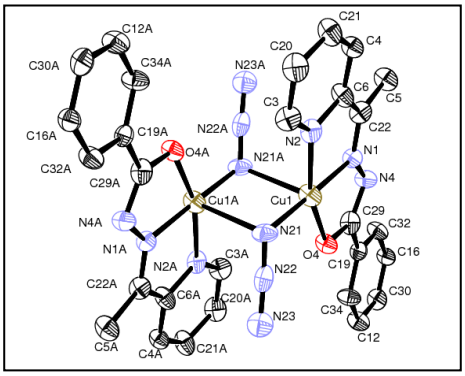
The next two double $\mu_{1,1}$ azide-bridged dinuclear copper (II) complexes [Cu_2(DMPTD))(μ_2-N_3)$_2$(N_3)] (**18**), [Cu_2(DBITD)(μ_2-N_3)$_2$$Cl_2$]. H_2O (**19**), [(DMPTD = 2,5-bis((pyridylmethy1)thio) thiadiazole, DBITD = 2,5-bis(benzimidazolylmethyl)thio)thiadiazole, PAP = 1,4-bis(2'-pyridylamino)phthalazine, PPD3Me = 3,6-bis(3'-methyl-1'-pyrazolyl)pyridazine), PPD = 3,6-bis(1'- pyrazoly1)pyridazine) show ferromagnetic interaction which can be explained from their structural parameters [44].

Another doubly end on bridged dinuclear copper(II) complex $[Cu(L5)(N_3)_2]_2$ (**20**) [L5 = 1-(2-aminoethyl)piperidine] (Table 2) show antiferromagnetic interaction despite of small Cu-N-Cu angle 98.85 (< 104°). Like **14** and **15** here also the azide ion binds the two copper centres in basal-apical fashion so the Cu-N_3-Cu angle can not explain the nature of magnetic interaction other structural parameters(like Cu-Cu separation Cu-N_3 distance, deviation of copper ions from the basal plane) have to be considered to explain the interaction [46].

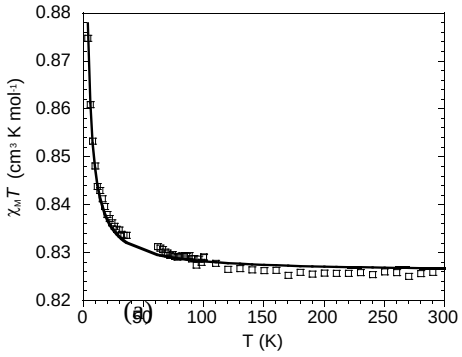
Table 2. Structural and magnetic parameters for asymmetric double end on (μ-$_{1,1}$-N_3) azido bridged transition metal complexes

Compounds	Cu-Cu(Å)	Cu-N(Å)	Cu-N-Cu(°)	J(cm^{-1})	Ref.
$[CuL1(N_3)]_2$(**14**)	3.193	2.039	90.50	-1.8	30
$[CuL_2(N_3)]_2$ (**15**)	3.161	2.020	86.82	-3.1	30
$[CuL_3(N_3)]_2$ (**16**)	3.318	2.060	93.60	0.26	30
$[Cu_2(L4)\ (N_3)_2](ClO_4)_2]$ (**17**)	-	-	-	-	45
$[Cu_2(DMPTD))(\mu_2\text{-}N_3)_2(N_3)]$ (**18**)	3.076	1.995, 1.966	101.9	85	44
$[Cu_2(DBITD)(\mu_2\text{-}N_3)_2Cl_2].\ H_2O$ (**19**)	-	-	-	47	44
$[Cu_2(L5)_2(N_3)_2]$(**20**)	3.348	2.016	98.85	-3.06	46
$[Cu_2(L6)_2(N_3)_2]$ (**21**)	3.205	1.968, 2.534	89.9	0.75	47
$[Cu(L7)(N_3)_2]_2$ (**22**)	3.180	1.998, 2.505	89.1	-8.9	48
$[Cu_2(L8)_2(N_3)_2]$ (**23**)	3.1122	2.035, 2.311	91.24	-0.22	49

Our group has reported a double end-on azide bridged dinulear copper(II) complex $[Cu_2(L6)_2(\mu_{1,1}\text{-}N_3)_2]$ (**21**) (Fig. 1), [where L6 = $C_6H_5C(O)NHN{=}C(CH_3)C_5H_4N$] [47] which show weak ferromagnetic interaction with J = +0.75 cm^{-1}. The two copper atoms of the dinuclear unit are linked by two azido bridging ligands in an end-on fashion. The copper atoms are in square planar geometry and, the bridging nitrogen atom of each azido ligand being in equatorial position of one copper; whereas it is in the axial position of the second copper. The weak coupling may be explained as follows: the magnetic orbital describing the unpaired electron on a copper(II) ion in square pyramid is of the $d_{x^2-y^2}$ type (the x and y axes being defined by the short equatorial bonds). The overlap between the magnetic orbitals of two neighbouring coppers is thus very small, and the isotropic interaction parameter (roughly proportional to the square of this overlap) is expected to be small.



(a)



(b)

Fig. 1: (a) ORTEP diagram of Complex **21**; (b) Experimental (□) and calculated (—) temperature dependence of $\chi_M T$ for **21** [47].

A rare asymmetric end-on double azido-bridged copper(II) complex$[Cu_2(L7)_2(N_3)_2]$ (**22**)(L =1-(*N*-salicylideneamino)-2-aminoethane) [48] with Cu−N(azide)−Cu angle in this complex is calculated to be 89.1°. This is unusually low in comparison to the same angle in other reported end-on azido-bridged binuclear complexes. Though a strong ferromagnetic interaction between the metal centers is expected in the complex, the coupling has actually been found to be antiferromagnetic, instead. To estimate the magnitude of the antiferromagnetic coupling the magnetic susceptibility data (T>20 K) were fitted to the modified Bleaney– Bowers equation for two interacting copper(II) ions S=1/2 with the Hamiltonian in the form $H = -J\hat{S}_1 \cdot \hat{S}_2$. The probable cause for this unusual magnetic behaviour can be explained similarly as the magnetic orbitals describing the single electron on two copper are mainly of $dx^2 - y^2$ type extended along the basal plane of the copper ions. The azido group connecting the two copper through an end-on bridge, azide

nitrogen atom occupies the basal position of one Cu but axial coordination position of square pyramidal geometry of another Cu atom. Consequently the interaction between magnetic orbitals of the two copper (II) ions is expected to be very weak leading to a small exchange coupling parameter. Besides, the Cu–N_3 distance [2.505**Å**] is significantly higher than the cut-off distance (2.05 **Å**) for the interaction being ferromagnetic. Another asymmetric bis-($\mu_{1,1}$-azido) bridged dinuclear copper(II) complex $[Cu_2(L8)_2(N_3)_2]$ (**23**) [where HL8= 2-((3-(methylamino)propylimino)methyl)-6-methoxyphenol], [49] shows antiferromagnetic exchange interactions with $2J = -0.45$ cm^{-1}. The magnetic field-dependent magnetization study (M − H) reveals existence of antiferromagnetic ordering at a lower temperature (2 K) with a very small coercive field (~20 Oe) suggesting soft magnet behavior of the complex.

3. Conclusion

The above review again proves that azido bridged copper(II) complexes are very much interesting for their versatile magnetic behaviour. Depending on the nature of the bridging mode and other structural parameters end on azido bridged dinuclear copper(II) complexes show ferromagnetic or antiferromagnetic interaction. Though complexes having large Cu-N_3-Cu angle (> 104°) exhibits antiferromagnetic interaction but many complexes show exceptional behaviour. This is because when the azide ligand bridges the metal centres in basal-basal fashion then only the magnitude of the Cu-N_3-Cu angle dictates the nature of interaction. But when azide ion bridges asymmetrically the two metal centres in basal-apical fashion then other structural parameters have to be considered to explain the nature of magnetic interaction. From this review it can be concluded that azide ion is very good bridging ligand and depending on the nature of the coligand it can propagates the magnetic interaction very efficiently and can produce interesting magnetic materials.

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