

CHAPTER 8

Crystal Structure and Magnetic Properties of a Hexacopper(II)-Based Azide-Bridged One-Dimensional Coordination Polymer: A New Pattern of Azide-Bridged Network

8.1. Introduction

Coordination polymers are the metal containing supramolecules which are generated due to coordinate bonds between metal ions and organic¹⁻⁷ or inorganic⁸⁻³¹ bridging ligands. Regarding inorganic bridging ligands to form varieties of coordination polymers, azide,^{8,11-18,19} cyanate,^{19,20} tetra^{21,22}/ hexa^{9,23-26}/ octa^{27,28} cyanometalates, dicyanamide,^{10,29-31} and sulphate³² may be mentioned as some most potential examples.

Azide is a versatile ligand.^{8,11-18,19,33-46} It can be a monodentate terminal ligand or it can behave as a bridging ligand in various modes, like end-on ($\mu_{1,1}$ -, commonly expressed as EO),^{8,11,12,14,17,33,34-40,41,42} end-to-end ($\mu_{1,3}$ -, commonly expressed as EE),^{8,11,13,15,16,18,19,33,43,44} $\mu_{1,1,1}$ -,^{11,12} $\mu_{1,1,3}$ -,¹⁴ $\mu_{1,1,1,1}$ -,⁴⁵ and $\mu_{1,1,3,3}$ -;⁴⁶ of which the first two types are the most common. With these coordination / bridging modes, several metallo–azide compounds have been reported which are either discrete compounds of varying nuclearity (di/tri/tetra/penta/etc.) or coordination polymer of varying dimensionality (1-D/2-D/3-D).^{8,11-18,19,33-46} As azide is a strong coupler of magnetic exchange interactions, metallo–azide species are also interesting members in molecular magnetism; a number of experimental^{8,34,37,43} and theoretical⁴⁷⁻⁵⁰ magneto-structural correlations have been determined in metallo-azide systems and a number of metallo-azide magnetic materials,^{8,13,16,35,36} including single molecule magnets³⁶ have been developed.

Although much research has been carried on metallo–azide systems, one problem in this area is that, it is difficult to control the composition and nuclearity of the final product and the problem is associated probably to the possibility of several coordination/bridging modes of azide. In fact, the nature of final product depends on some subtle effect governed by the nature of metal ion, solvent, blocking organic ligand, etc. Due to this uncertainty, the area of metallo–azide systems is yet very green. Therefore, we have been motivated to explore the metallo–azide systems and isolated a 1-D copper(II)–azide compound of composition $[\text{Cu}^{\text{II}}_6(\text{N}_3)_6]$

$\text{diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**). Herein, synthesis, characterization, crystal structure and magnetic properties of **35** are described.

8.2. Experimental Section

Caution! Azide complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

8.2.1. Materials and Physical Methods

All the reagents and solvents were purchased from commercial sources and used as received. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded from KBr disks of the samples over the range 400–4000 cm^{-1} on a Bruker-Optics Alpha-T spectrophotometer. Magnetic measurements were carried out in the “Unitat de Mesures Magnètiques (Universitat de Barcelona)” on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic fields used were 0.03 (from 2 K to 30 K) and 1.0 T (from 2 K to 300 K).

8.2.2. Synthesis

$[\text{Cu}^{\text{II}}_6(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**). A methanol solution (15 mL) of N,N-diethylethylenediamine (0.038 mg, 0.33 mmol) was dropwise added to a methanol solution (10 mL) of copper(II) perchlorate hexahydrate (0.367 g, 1 mmol). To the resulting blue-violet solution was added sodium azide (0.13 g, 2 mmol) dissolved in minimum volume of water. A brown precipitate formed immediately. The stirring was continued for 10 minutes. Then the mixture was filtered and the green filtrate was kept at room temperature for slow evaporation. After a few days, brown rod-shaped crystalline

compound having diffraction quality single crystals was deposited. The compound was collected by filtration and washed with methanol.

8.2.3. Analytical and FT–IR Data

For **35**: Anal. Calcd. for $C_6H_{16}N_{20}Cu_3$: C, 12.89; H, 2.88; N, 50.12%. Found: C, 12.54; H, 3.02; N, 50.28%. FT-IR on KBr (cm^{-1}): ν (azide), 2106 vs and 2063 vs.

8.2.4. Crystal Structure Determination of $[Cu^II_6(N,N\text{-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**)

The crystallographic data for **35** are summarized in Table 8.1. Diffraction data were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). For data processing and absorption correction the packages SAINT⁵¹ and SADABS⁵¹ were used. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXTL⁵² and SHELXL-97⁵³ packages. The N–H hydrogen atoms in **35** were located from difference Fourier maps. All other hydrogen atoms in **35** were inserted at calculated positions with isotropic thermal parameters. The nonhydrogen and hydrogen atoms were refined, respectively, anisotropically and isotropically. The final refinement converged to the R_1 value ($I > 2\sigma(I)$) 0.029.

Table 8.1. Crystallographic Data for **35**.

empirical formula	C ₆ H ₁₆ N ₂₀ Cu ₃
fw	559.01
crystal system	monoclinic
space group	<i>P2₁/n</i>
<i>a</i> (Å)	7.6098(6)
<i>b</i> (Å)	20.8173(18)
<i>c</i> (Å)	12.5742(11)
α (deg)	90.00
β (deg)	101.872(3)
γ (deg)	90.00
<i>V</i> (Å ³)	1949.3(3)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.905
μ (mm ⁻¹)	3.285
<i>T</i> (K)	296(2)
<i>F</i> (000)	1116
2 θ (deg)	3.84–64.00
Index ranges	–11 ≤ <i>h</i> ≤ 10 –29 ≤ <i>k</i> ≤ 30 –18 ≤ <i>l</i> ≤ 17
Reflections collected	28593
Independent reflections(<i>R</i> _{int})	6620 (0.0305)
Parameters refined	272
Goodness-of-fit on <i>F</i> ²	0.989
<i>R</i> ₁ ^{<i>a</i>} , w <i>R</i> ₂ ^{<i>b</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0294/0.0753
<i>R</i> ₁ ^{<i>a</i>} , w <i>R</i> ₂ ^{<i>b</i>} (for all data)	0.0453/0.0814

$$^a R_1 = [\sum ||F_o| - |F_c|| / \sum |F_o|].$$

$$^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}.$$

8.3. Results and Discussion

8.3.1. Description of the Structure of $[\text{Cu}^{\text{II}}_6(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**)

The crystal structure of **35** is shown in Figure 8.1. This compound is a one-dimensional azide-bridged tape-type polymer of copper(II). The structure contains three types of azide ligands: $\mu_{1,1}\text{-}$ (EO), $\mu_{1,3}\text{-}$ (EE), and $\mu_{1,1,1}\text{-}$. There are three crystallographically different copper(II) centers: Cu1, Cu2 and Cu3. Among these, Cu1 is coordinated to two nitrogen atoms of the diamine, N,N-diEten, and three nitrogen atoms of two $\mu_{1,1}\text{-}$ and one $\mu_{1,3}\text{-}$ azide ligands. In contrast to Cu1, Cu2 and Cu3 are not coordinated to diamine but these two are pentacoordinated with five azide nitrogen atoms. Cu2 is coordinated with four $\mu_{1,1}\text{-}$ and one $\mu_{1,1,1}\text{-}$ azide nitrogen atoms, while Cu3 is coordinated with five nitrogen atoms of two $\mu_{1,1}\text{-}$, two $\mu_{1,1,1}\text{-}$ and one $\mu_{1,3}\text{-}$ azide ligands. The coordination environments of the three types of copper(II) centers are shown in Figure 8.2.

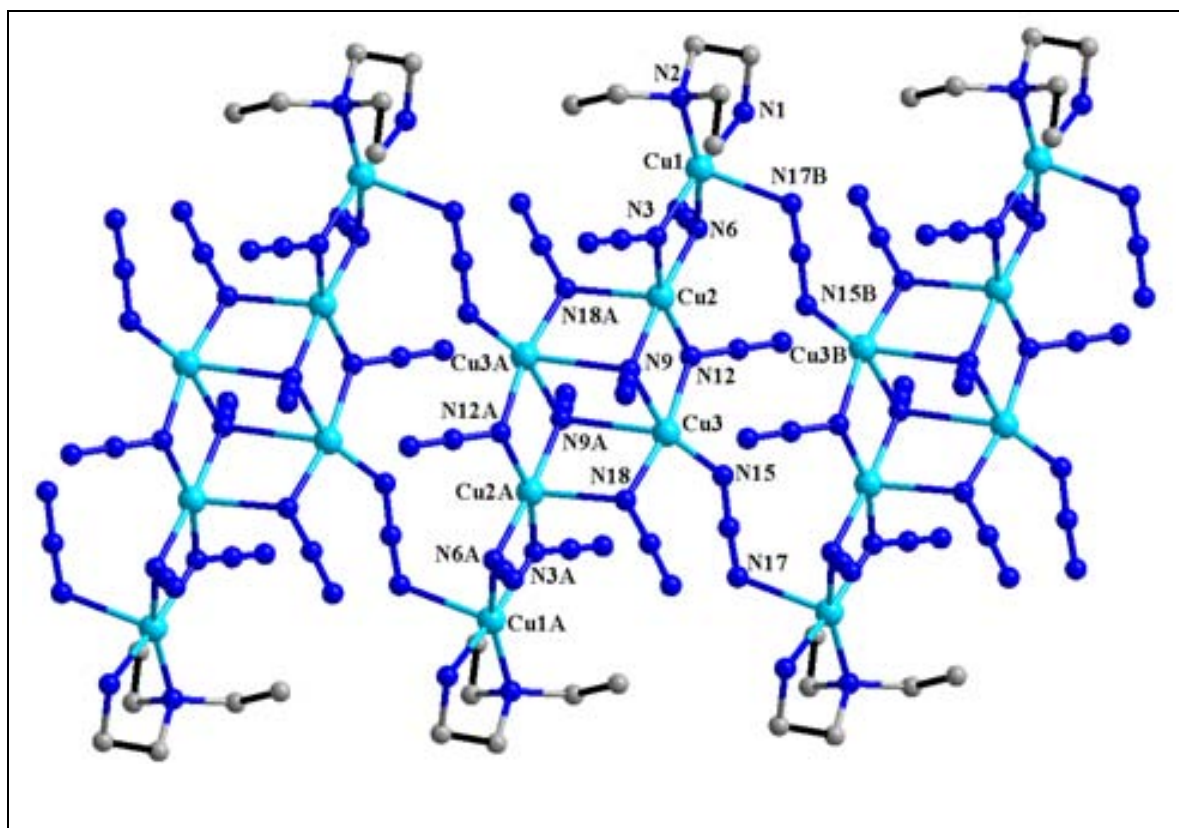


Figure 8.1. Crystal structure of the one-dimensional tape-polymer $[\text{Cu}^{\text{II}}_6(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**). All hydrogen atoms are omitted for clarity. Symmetry: A, $1-x, -y, 2-z$; B, $2-x, -y, 2-z$.

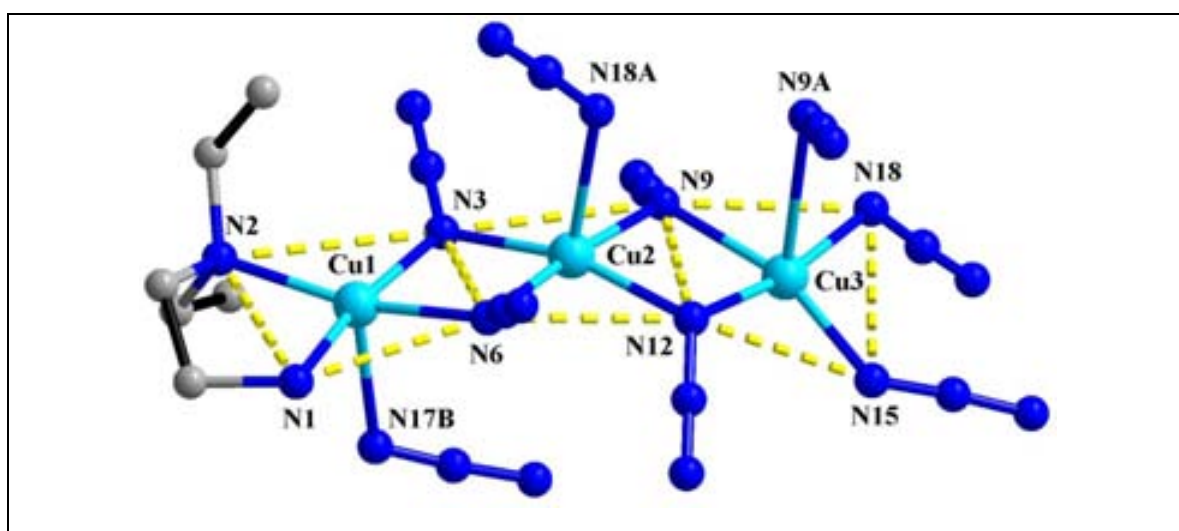


Figure 8.2. Coordination environments of the three types of copper(II) centers in $[\text{Cu}^{\text{II}}_6(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**). The dotted lines indicate the basal planes.

The compound **35** may be considered as a hexacopper(II)-based one-dimensional polymer. The hexacopper(II) units, in turn, may be considered as a tetracopper(II) cyclic unit (Cu₂Cu₃Cu₂ACu₃A) and two other copper(II) centers. One metal ion (Cu₂) of a tetracopper(II) unit is bridged with the fifth copper(II) ion (Cu₁) and, obviously, Cu₂A of the tetracopper(II) unit is bridged with the sixth copper(II) ion (Cu₁A) to form the hexacopper(II) building block. The adjacent metal ions (Cu₂Cu₃, Cu₃Cu₂A, Cu₂ACu₃A, Cu₃ACu₂) in the tetracopper(II) cyclic unit are bridged by one $\mu_{1,1}$ - and one $\mu_{1,1,1}$ - azide ligands and a diagonal pair (Cu₃Cu₃A) is bridged by two $\mu_{1,1,1}$ - azide ligands, while there is no direct bridging moiety between the metal ions of the second diagonal pair (Cu₂Cu₂A). Cu₂ and Cu₂A of the tetracopper(II) cyclic unit are bridged with Cu₁ and Cu₁A by double $\mu_{1,1}$ - azide ligands, to generate the hexacopper(II) unit. One hexacopper(II) unit is interlinked with a neighboring such unit by two $\mu_{1,3}$ - azide ligands along one side and, evidently, with another neighboring such unit in the second side by two other $\mu_{1,3}$ - azide ligands to generate a one-dimensional network along the crystallographic *a* axis. It is worth mentioning at this point that the hexacopper(II) basic unit in **35** may also be considered as a dimer of two approximately linear trinuclear units, Cu₁Cu₂Cu₃ and Cu₁ACu₂ACu₃A; the Cu₁Cu₂Cu₃ angle being 160.76°.

All the copper(II) centers in **35** (Cu₁, Cu₂ and Cu₃) are pentacoordinated and the pentacoordinated environment is distorted square pyramidal (Figure 8.2), as evidenced by the τ values 0.113 (Cu₁), 0.209 (Cu₂) and 0.107 (Cu₃). The apical position for Cu₁, Cu₂ and Cu₃ in **35** is occupied by the $\mu_{1,3}$ - azide nitrogen atom N17B, $\mu_{1,1}$ - azide nitrogen atom N18A and $\mu_{1,1,1}$ - azide nitrogen atom N9A, respectively.

Selected bond lengths and angles in the coordination environment of the copper(II) centers in **35** are listed in Table 8.2. The values are typical of distorted square pyramidal copper(II) centers. The Cu–N–Cu bridge angles involving $\mu_{1,1}$ - and $\mu_{1,1,1}$ - azide ligands in **35** are 100.49, 100.76, 101.63 and 101.65° and 91.97, 97.88 and 100.59°.

Table 8.2. Selected Bond Lengths (Å) and Bond Angles (°) of Compound **35**.

Cu1–N1	1.980(2)	N3–Cu2–N6	80.05(6)
Cu1–N2	2.058(1)	N3–Cu2–N9	102.88(6)
Cu1–N3	2.018(1)	N3–Cu2–N18A	101.44(6)
Cu1–N6	2.030(1)	N6–Cu2–N12	94.79(6)
Cu1–N17B	2.361(2)	N6–Cu2–N18A	97.41(6)
Cu2–N3	1.998(1)	N9–Cu2–N18A	86.01(6)
Cu2–N6	1.978 (1)	N9–Cu2–N12	81.22(6)
Cu2–N9	1.999 (1)	N12–Cu2–N18A	95.80(7)
Cu2–N12	1.983(1)	N9–Cu3–N15	161.57(8)
Cu2–N18A	2.347(2)	N12–Cu3–N18	168.03(7)
Cu3–N9	2.082(1)	N9–Cu3–N12	79.09(6)
Cu3–N12	1.988(1)	N9–Cu3–N18	94.70(7)
Cu3–N15	1.954(2)	N9–Cu3–N9A	79.40(5)
Cu3–N18	1.943(2)	N18–Cu3–N15	98.76(7)
Cu3–N9A	2.602(1)	N18–Cu3–N9A	80.34(6)
Cu1…Cu2	3.088	N12–Cu3–N15	89.69(7)
Cu2…Cu3	3.078	N12–Cu3–N9A	88.41(6)
N2–Cu1–N6	162.29(6)	N15–Cu3–N9A	115.16(7)
N1–Cu1–N3	169.06(6)	Cu1–N3–Cu2	100.49(7)
N1–Cu1–N2	86.81(6)	Cu1–N6–Cu2	100.76(6)
N1–Cu1–N17B	89.16(8)	Cu2–N9–Cu3	97.88(6)
N1–Cu1–N6	90.73(7)	Cu2–N12–Cu3	101.63(7)
N2–Cu1–N17B	103.96(6)	Cu3–N9–Cu3A	100.60(6)
N2–Cu1–N3	103.81(6)	Cu3–N9A–Cu2A	91.97(6)
N3–Cu1–N6	78.36(6)	Cu3– N18–Cu2A	101.65(7)
N3–Cu1–N17B	90.77(7)	Cu1–N17B– N16B	115.27(14)
N6–Cu1–N17B	93.53(6)	Cu3– N15– N16	128.90(16)
N3–Cu2–N12	162.48(7)	Cu1–N17B…N15B–Cu3B	113.07
N6–Cu2–N9	175.02(7)	Cu3–N15…N17–Cu1	–113.07

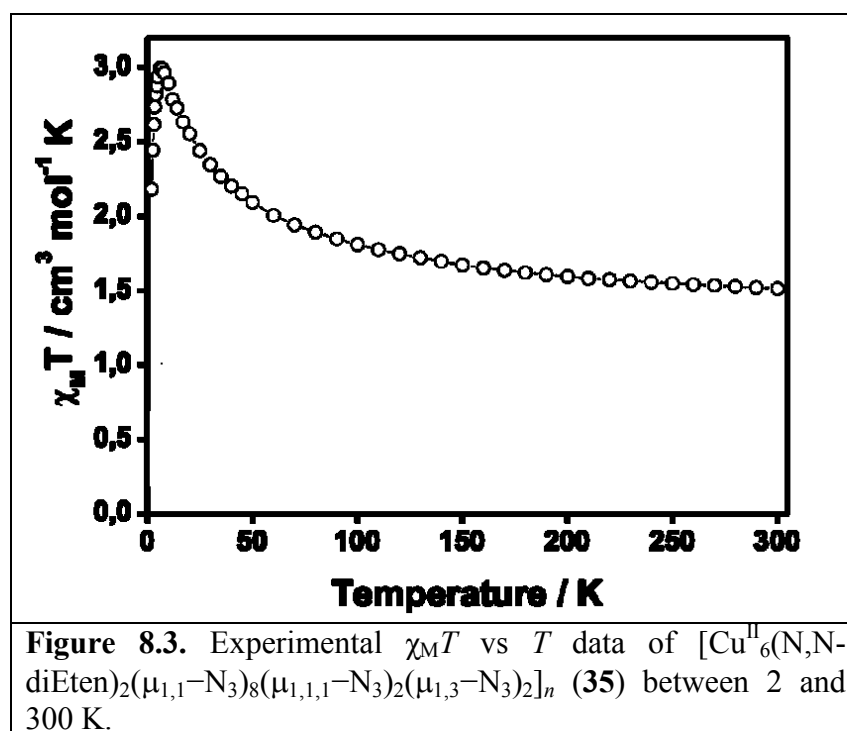
8.3.2. Comparison of Composition/Structure of **35** with Related Systems

There are three compounds in the literature containing copper(II), azide and N,N-diEten. Those are two double $\mu_{1,1}$ - azide bridged dinuclear compounds $[\text{Cu}^{\text{II}}_2(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2]$ (**I**)³⁹ and $[\text{Cu}^{\text{II}}_2(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_2(\text{NCO})_2]$ (**II**)⁴⁰ and a one-dimensional compound $[\text{Cu}^{\text{II}}_2(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2][\text{Cu}^{\text{II}}(\text{N,N-diEten})(\mu_{1,3}\text{-N}_3)(\text{N}_3)]_n$ (**III**).¹⁷ Clearly, **35** is an entirely different compound in comparison to **I**, **II** or **III**. Now, let us mention whether the one-dimensional topology in **35** is of a new type or a known type. Previously, a few hexacopper(II)-based copper(II)-azide one-, two- and three-dimensional compounds containing a diamine have been reported.¹²⁻¹⁴ The ratio of Cu^{II} :diamine:azide in all those compounds is 1:0.33:2, as in **35**. But, not only in the previously reported two-/three-dimensional compounds but also in the one-dimensional compounds, the relative positioning of the six copper(II) ions in the basic Cu^{II}_6 unit are different from those in **35**. The number and type of azide bridges that interlink the neighboring hexacopper(II) units are also different in **35** in comparison to the reported examples. The network-topology in **35** is new among a few previously reported hexacopper(II)-based coordination polymers and also among metallo-azide systems of any metal ions.

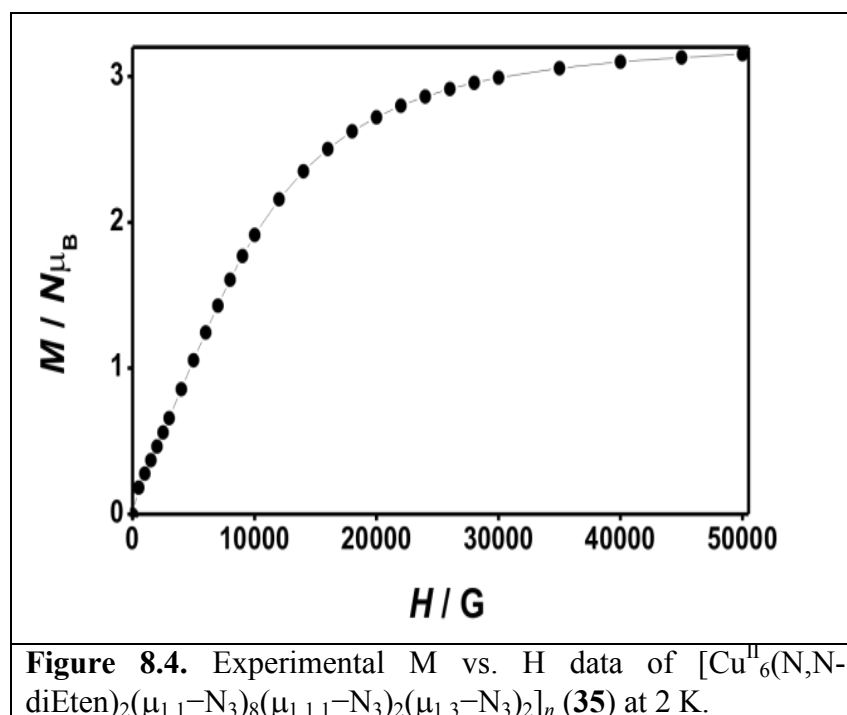
Synthesis procedure of **III** has not been reported. On the other hand, although synthesis procedure of **I** and **II** has been reported, the latter compound contains cyanate as an additional ligand and so comparison of it with **35** in terms of synthesis procedure is not required. So, let us see what are the similarities/differences in the synthesis procedure of **35** and **I**: (i) Solvent is ethanol (plus slight water) for **I** but methanol (plus slight water) for **35**; (ii) Sodium azide is added to the mixture of Cu^{II} and diamine in both; (iii) The ratio of $\text{Cu}^{\text{II}}:\text{N}_3^-$ is 1:2.2 for **I** but 1:2 for **35**; (iv) The ratio of $\text{Cu}^{\text{II}}:\text{N,N-diEten}$ is 1:1 for **I** but 1:0.33 for **35**. Among these, (i), (ii), and (iii) are same or practically same, while (iv) is different. Clearly, dinuclear compound **I** and hexacopper(II)-based 1-D compound **35** are formed due to the change of stoichiometric ratio of the metal ion and the diamine blocking ligand.

8.3.3. Magnetic Properties

Solid-state, variable-temperature magnetic susceptibility data using 0.03 and 1.0 T fields were collected on polycrystalline sample of compound **35**. The resulting data are plotted as $\chi_M T$ vs T and M vs H in Figure 8.3. $\chi_M T$ increases with decreasing temperature, showing an overall ferromagnetic behavior. As already discussed, hexacopper(II) basic unit in **35** may be considered as dimer-of-tricopper(II) units, so we have plotted $\chi_M T$ and M values per Cu^{II}_3 unit.



Compound **35** exhibits a $\chi_M T$ value at 300 K of $1.51 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, higher to that expected for a magnetically isolated trinuclear Cu^{II} system (where $\chi_M T = 1.125 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $S = \frac{1}{2}$ and assuming $g = 2.0$). This value rises smoothly from room temperature until $\sim 50 \text{ K}$ ($2.09 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) and rapidly increases reaching a value of $3.00 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 5.5 K , followed by a drastic drop up to 2 K ($2.18 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$; Figure 8.3.). M vs H data matches well with the idea of three Cu^{II} ions, reaching rapidly saturation and supporting a global ferromagnetic exchange (Figure 8.4).



The already described bridging patterns in **35** provide several pathways for the metallic centers to magnetically communicate. Interestingly, the ferromagnetic behavior can be well-described by relating the magnetic orbitals involved in the different exchanges and the bridging ligand modes. In the closely linear trinuclear Cu1Cu2Cu3 units in **35**, Cu1 and Cu2 are bridged by two $\mu_{1,1}\text{-}$ azide bridges and Cu2 and Cu3 are bridged by one $\mu_{1,1}\text{-}$ and one $\mu_{1,1,1}\text{-}$ azide bridges. Each of all these bridging nitrogen atoms occupy equatorial positions of the metal ion and the $\text{Cu}\text{-azide}\text{-Cu}$ angles involving these equatorial-equatorial (eq-eq) $\mu_{1,1}\text{-}/\mu_{1,1,1}\text{-}$ azide groups lie in the range $100.49\text{-}101.63^\circ$. As the occupation mode of the $\mu_{1,1}\text{-}/\mu_{1,1,1}\text{-}$ azide groups is eq-eq, the magnetic orbital for each copper(II) in the exchange pathway in the trinuclear unit is $d_{x^2-y^2}$. In addition, the bridge angle values ($100.49\text{-}101.63^\circ$) lie well below 108° .³⁷ So, the metal centers in the trinuclear unit are expectedly coupled by strong ferromagnetic interaction, J_1 .^{8,33,34,36,37} The two trinuclear moieties (Cu1Cu2Cu3 and Cu1ACu2ACu3A) form a dimer due to the interlinking by $\mu_{1,1}\text{-}/\mu_{1,1,1}\text{-}$ azide bridges. Although the bridge angles ($91.97\text{-}101.65^\circ$) in these cases also lie well below 108° ,³⁷ the occupation mode for each of these azide nitrogen atom is equatorial-axial (eq-ax), i.e., the magnetic orbitals for a

pair of metal ions is $d_{x^2-y^2}$ and d_z^2 , providing most likely ferromagnetic interactions (J_2), although much weaker in nature than the previous. The tetracopper(II) units are interlinked by $\mu_{1,3}$ - azide ligands which usually mediate antiferromagnetic interaction.^{8,33,43,44} However, as the occupation mode of these $\mu_{1,3}$ - azide nitrogen atoms is also eq-ax, i. e., the magnetic orbitals for a pair of metal ions is $d_{x^2-y^2}$ and d_z^2 , the exchange interaction (J_3) should also be small in this route. Presumably, due to the small values of J_2 and J_3 , one could simplify (magnetically speaking) such complex system, assuming these two exchanges almost zero, and fitting the magnetic susceptibility data using a linear trinuclear expression. However, all our efforts in this direction did not reproduce the experimental data and provided unrealistic values.

Herein the ferro- and/or antiferromagnetic nature of the magnetic exchanges have been described taking into account the overall ferromagnetic behavior of the compounds as well as the general rules applied to metal centers, coordinated through azide bridges where $\mu_{1,1}$ - azido groups provide most likely ferromagnetic interactions^{8,33,34,36,37} and $\mu_{1,3}$ - azido bridges antiferromagnetic ones^{8,33,43,44} and so, the experimental data can be well explained. Nevertheless, it is possible to find reverse situations.^{15,18,41-43} For one such reverse situation, it is worth mentioning that previous studies have shown that the nature of the coupling parameter in end-to-end azide bridged systems depends on the M-N-N angles and the M-N...N-M torsion angles.^{15,18,43} Regarding this matter, the $\mu_{1,3}$ -bridging modes of the azide ligand for **35** involve $d_{x^2-y^2}$ and d_z^2 orbitals, diminishing the antiferromagnetic component of the exchange coupling. Also, as the Cu-N-N angles (115.3 and 128.9°; Table 8.2) are larger than 108° and their torsion angles (113.07°; Table 8.2) differ from 180°, it is possible that the magnetic exchange would be ferromagnetic in nature too.^{15,18,43} For another reverse situation, it may be mentioned that the exchange interaction propagated through eq-ax $\mu_{1,1}$ - azide bridge may be either ferromagnetic or antiferromagnetic but the in-depth reason or correlation is yet lacking.^{41,42} Therefore, a more accurate study would require theoretical calculations to reproduce precisely the nature of each exchange.

8.4. Conclusions

Three copper(II)–azide compounds with N,N-diethylethylenediamine have been reported previously. But, on changing stoichiometric ratio of copper(II) and diamine a new compound of composition $[\text{Cu}^{\text{II}}_6(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**) has been generated. Interestingly, a new type of azide bridging network pattern is observed in the structure of **35**.

Cryomagnetic properties of **35** reveal that it exhibits overall ferromagnetic interaction, which has been explained qualitatively in terms of the nature of azide bridge (end-on, end-to-end, etc.), bridging mode with respect to occupation of coordination sites (eq-eq/eq-ax), Cu–N–Cu/Cu–N–N angles, Cu–N⋯N–Cu torsion angles along with known magneto-structural correlations.

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