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Polyhedron 25 (2006) 2764–2772

Copper(II) azide complexes of 1-alkyl-2-(arylazo)imidazoles: Structure and magnetism

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Received 15 February 2006; accepted 2 April 2006 Available online 27 April 2006

Abstract

Tetranuclear Cu(II)-azido complexes of the composition $[Cu(RaaiR')(N_3)_2]_4$ have been synthesized by reacting 1-alkyl-2-(arylazo)imidazole (RaaiR'), Cu(OAc)_2 · H₂O and NaN₃ in 1:1:2 mole proportion [RaaiR'; R = H (3), Me (4); R' = Me (a), Et (b)]. The structure of $[Cu(HaaiMe)(N_3)_2]_4$ (**3a**) has been confirmed by an X-ray diffraction study. The tetranuclear copper core is generated by dimerisation via $\mu_{1,1}$ -N₃ of two dimer units. In each dimer one copper centre is five-coordinated (CuN₅) and the other one is six-coordinated (CuN₆). Variable temperature magnetic measurements of **3a** show the occurrence of ferromagnetic ($J_1 = +25.3 \text{ cm}^{-1}$) and antiferromagnetic ($J_2 = -4.7 \text{ cm}^{-1}$) interactions through the double and single end-on azido bridges, respectively. Upon addition of excess ligand, a 2-methoxy ethanol solution of the tetranuclear complex fragmented into a mononuclear copper(II) complex of the formula [Cu(RaaiR')₂(N₃)₂], and in one case, [Cu(HaaiEt)₂(N₃)₂], the structure was established by X-ray diffraction. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Copper(II)-azide; 1-Alkyl-2-(arylazo)imidazoles; Tetranuclear; Magnetic properties

1. Introduction

Polynuclear metal complexes are of contemporary interest [1–7]. A careful selection of ligand, metal centre and reaction conditions can confer control over the topology of the resulting framework [8–10]. Pseudohalides, especially azide, are versatile polyatomic bridging units that can bind metal ions via end-on (EO, $\mu_{1,1}$) and end-to-end (EE, $\mu_{1,3}$) motifs [11] with novel magnetic properties. This leads to extreme structural and electronic versatility allowing ferromagnetic (F) or antiferromagnetic (AF) coupling via EO and EE bridges, respectively, and tunes magnetic behaviors via modification of the bond parameters, in particular in the bridging region [12]. Different organic

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blockers [12,13] of varied denticities have been used to prepare such molecular architectures. Multidentate Schiff base ligands [12] and polyamines [13] have generally been used to stabilize the core unit. Use of the azo function in this direction has rarely been explored [14].

We have been engaged for some time in exploring the chemistry of 1-alkyl-2-(arylazo)imidazole with transition and non-transition metal ions [14–21]. Our understanding of copper complexes with arylazoimidazole has mainly focused on the structural, spectroscopic and electrochemical properties of copper(I) complexes. Attempts to synthesize copper(II)–RaaiR' have failed even under aerobic conditions in the presence of Cl⁻ or ClO₄⁻ as counter ions, and [Cu(RaaiR')₂]⁺ has been crystallized [15]. However, the presence of N₃⁻ or NCS⁻ in the reaction mixture has enabled Cu(II) complexes to be stabilized [16]. Towards the preparation of multinuclear copper(II) complexes via

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^{0277-5387/\$ -} see front matter @ 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2006.04.007

self-assembly of metal, bidentate azoimine blocker and pseudohalide, we have been successful in isolating and characterizing tetranuclear complexes with the formula $[Cu(RaaiR')(N_3)_2]_4$ [RaaiR'; R = H (3), Me (4); R' = Me (a), Et (b)]. The structure has been confirmed by a single crystal X-ray diffraction study of $[Cu(HaaiMe)(N_3)_2]_4$ (3a). Variable temperature magnetic measurements of 3a show the occurrence of ferromagnetic $(J_1 = +25.3 \text{ cm}^{-1})$ and antiferromagnetic $(J_2 = -4.7 \text{ cm}^{-1})$ interactions through the double and single end-on azido bridges, respectively. Addition of excess of RaaiR' to the respective tetranuclear copper(II) complex in 2-methoxy ethanol has enabled the cluster to be split into a mononuclear copper(II) complex of the composition $[Cu(RaaiR')_2(N_3)_2]$. The structure and magnetism are detailed below.

2. Results and discussion

2.1. The complexes

The complexes are synthesized by the reaction of 1alkyl-2-(arylazo)imidazole (RaaiR'), $Cu(OAc)_2 \cdot H_2O$ and NaN₃ in MeOH in a 1:1:2 mole proportion at 298 K. The ligand is an unsymmetric, N,N'-bidentate chelator where N and N' refer to N(imidazole) and N(azo) donor centres, respectively. The azide (N_3^-) is a bridging ligand showing its versatile coordination motifs. The composition, $[Cu(RaaiR')(N_3)_2]_4$ (R = H (3), Me (4); R' = Me (a), (b)) has been confirmed by X-ray crystal structure determination of one of the compounds, $[Cu(HaaiMe)(N_3)_2]_4$ (3a). The tetranuclear cluster is dissociated into a mono-copper complex, $[Cu(RaaiR')_2(N_3)_2]$ (5, 6) upon addition of excess of RaaiR' to a 2-methoxy ethanol solution of the complex. The structure of the mononuclear copper(II) compound has also been established by X-ray structure study in one case, $[Cu(HaaiEt)_2(N_3)_2]$ (6a), and by comparing with previously reported results [16].



2.2. Spectral studies

Infrared spectral data were assigned on comparing with the free ligand data and on comparing with [Cu(RaaiR')₂(N₃)₂] [16]. The most significant observation is the appearance of strong sharp stretches at 2069–2082, 2045–2050 and 2026–2028 cm⁻¹ for **3** and **4**. These correspond to $v_{asym}(N_3)$. This supports a bridging end-on type

binding of N₃ in the complexes **3** and **4** [9,11,22]. Moderately intense stretchings at 1583–1598 and 1438–1448 cm⁻¹ are due to v(C=N) and v(N=N), respectively [14].

Because of the insolubility of the complexes in common organic solvents, the electronic spectra of the complexes have been recorded in *N*,*N*-dimethyl formamide (DMF) solution in the UV–Vis region (200–900 nm). The complexes (**3**, **4**) exhibit four weak transitions around 715, 585, 475 and 450 nm. The position and intensity of the bands may not only be of d–d origin rather an admixture of d–d and MLCT ($d\pi(Cu) \rightarrow \pi^*(\text{ligand})$) transitions. The bands ≤ 400 nm are presumably due to intra-ligand $\pi - \pi^*$ and $n - \pi^*$ transitions.

2.3. Crystal structures

2.3.1. $[Cu(HaaiMe)(N_3)_2]_4$ (3a)

The X-ray structure (Fig. 1) reveals that complex **3a** is a neutral tetranuclear copper(II) derivative, comprising a dimer-of-dinuclear copper(II) subunits. Selected bond lengths and angles are given in Table 1. There are two crystallographically unique copper(II) environments; one of them is a five-coordinated square-based pyramid with a CuN₅ donor set and other is a six-coordinated distorted octahedral CuN₆ type. The dinuclear core unit is generated by a two $\mu_{1,1}$ -N₃ bridging scheme. Dimerisation of the dinuclear motif is carrying out by $\mu_{1,1}$ -N₃-group bridging. Thus, an arrangement of four copper atoms is formed. Each copper centre has been chelated with a HaaiMe ligand in which the ligand acts as an unsymmetric bidentate N,N'-donor type where N(imidazole) and N(azo) refer to N and N', respectively.

The atomic groups Cu(1), N(5), C(13), N(7), N(8) and Cu(2), N(1), C(3), N(3), N(4) constitute two chelate planes of mean deviation ≤ 0.02 Å. The pendant phenyl ring makes a dihedral angle of about 8° with the chelating



Fig. 1. ORTEP view of **3a** showing the metal environment and the atom labelling.

	Table 1				
$\mathbf{V}_{\mathbf{r}}$ = $\mathbf{r}_{\mathbf{r}}$	Calastad Is	 (Å)	 	(\mathbf{M}_{-})	(2-)

Selected bolid dista	nces (A) and	angles () for [Cu(Haanvie)	$(1N_3)_2]_4 (3a)$
Cu(1)-N(5)	2.002(2)	N(5)-Cu(1)-N(9)	168.06(10)
Cu(1)–N(8)	2.639(1)	N(5)-Cu(1)-N(12)	92.35(10)
Cu(1)-N(9)	2.017(2)	N(5)-Cu(1)-N(15)	97.47(10)
Cu(1)-N(12)	1.973(2)	N(9)-Cu(1)-N(12)	77.77(10)
Cu(1)-N(15)	1.961(3)	N(9)-Cu(1)-N(15)	93.52(10)
Cu(2)–N(1)	1.973(2)	N(12)-Cu(1)-N(15)	165.59(12)
Cu(2)–N(4)	2.632(3)	N(8)–N(7)–C(13)	113.2(3)
Cu(2)–N(9)	2.051(2)	Cu(1)-N(8)-N(7)	107.24
Cu(2)–N(12)	1.980(2)	Cu(1)–N(5)–C(13)	120.7(2)
Cu(2)-N(18)	1.967(3)	Cu(1)-N(15)-N(16)	122.6(2)
N(3)–N(4)	1.260(3)	N(1)-Cu(2)-N(9)	95.87(10)
N(1)–C(3)	1.325(4)	N(1)-Cu(2)-N(12)	169.23(11)
N(3)–C(3)	1.387(4)	N(1)-Cu(2)-N(18)	94.00(10)
N(7)–N(8)	1.243(4)	N(9)-Cu(2)-N(12)	76.82(10)
N(5)-C(13)	1.332(5)	N(9)-Cu(2)-N(18)	170.03(10)
N(7)–C(13)	1.372(5)	N(12)-Cu(2)-N(18)	93.21(11)
N(9)-N(10)	1.213(4)	Cu(2)-N(1)-C(3)	121.4(2)
N(10)-N(11)	1.168(5)	N(1)-C(3)-N(3)	128.1(3)
N(12)–N(13)	1.195(4)	N(15)-N(16)-N(17)	178.0(3)
N(13)-N(14)	1.126(5)	N(4)-N(3)-C(3)	112.0(3)
N(15)-N(16)	1.191(4)	Cu(1)-N(15)-Cu(2_a)*	100.59(12)
N(16)-N(17)	1.143(8)	Cu(1)–N(9)–N(10)	124.5(2)
N(18)-N(19)	1.182(4)	Cu(2)-N(9)-N(10)	127.2(2)
N(19)-N(20)	1.152(5)	N(9)-N(10)-N(11)	177.9(4)
$Cu(1) \cdot \cdot \cdot Cu(2)$	3.130	Cu(1)-N(12)-Cu(2)	104.71(12)
$Cu(1) \cdots Cu(2_a)^{\#}$	3.592	Cu(1)-N(12)-N(13)	131.3(2)
		Cu(2)-N(12)-N(13)	123.8(2)
		N(12)-N(13)-N(14)	177.8(3)
		N(8)-Cu(1)-N(9)	107.01(10)
		N(1)-Cu(2)-N(4)	69.54(9)
		N(5)-Cu(1)-N(8)	68.75(10)

[#] Symmetry code: 2 - x, 1 - y, 1 - z.

plane. The chelate angles of -Cu -N=N-C=N-N(1)-Cu(2)-N(4), 69.54(9)°, N(5)-Cu(1)-N(8), are $68.75(10)^{\circ}$. From the respective basal plane, the Cu(1) and Cu(2) centres are moved in same direction by -0.168(1) and -0.123(1) Å. These two planes are inclined at a dihedral angle of 87.22(10)°. In the dinuclear motif the bridging unit Cu₂N₂ is a four armed distorted plane of mean deviation ~ 0.02 Å. The Cu-N distances in the Cu_2N_2 unit reveal the distortion of the tetraatomic cycle: Cu(1)-N(1), 2.017(2); Cu(2)-N(1), 2.051(2); Cu(1)-N(12), 1.973(2); Cu(2)-N(12), 1.980(2) Å. The bridge angles are $100.60(11)^{\circ}$ and $104.71(12)^{\circ}$. The other two angles (N(9)-Cu(1/2)-N(12)) are 77.77(10)° and 76.82(10)°. The chelate and bridge planes are inclined at an angle of $76.30(13)^{\circ}$. Double bridged azide groups are inclined at an acute angle with the bridge plane [N(9)-N(10)-N(11)] makes 55° and N(12)–N(13)–N(14) makes 15° angle with Cu₂N₂]. The single-bridged azido group [N(15)-N(16)-N(17)] lies at an angle of 61° with the Cu₂N₂ motif. Dimerisation of the dicopper core generates the Cu₂N bridge unit $(Cu(2_a)^* -$ N(15)–Cu(1)) (* symmetry: 2 - x, 1 - y, 1 - z) of angle 106.59(12)°. The geometrical arrangement reflects the distorted orientation of the groups around the bridge. In the CuN₆ arrangement the donor centres are as follows: chelating HaaiMe gives two N-donor centres; three end-on azido bridged-N centres and a terminal azido-N donor. The bond

parameters around the CuN₆ coordination environment shows a distorted octahedral arrangement. In the TBP CuN_5 , the triangular base is constituted by N(8), N(13), N(15), Cu(1) and apical positions are occupied by N(9)and N(5). The azido bridge angles in the dinuclear copper(II) unit (Cu(1)–{ $\mu_{1,1}$ -N₃}₂–Cu(2)) are 100.60(11)° and 104.72(12)° and lie in the range of reported values [9,11,27]. The bridge angle has a major effect on the spinexchange phenomena (evaluated from the exchange parameter J). Planarity of the Cu_2N_2 unit, chelate angle of the capping agent, dihedral angle between two coordination planes, steric and electronic factors of the ligand significantly control the magnetic properties of the complexes. The two dinuclear copper(II) cores $(Cu(1) \cdots Cu(2) \text{ unit})$ are bridged by a $\mu_{1,1}$ -N₃ group in an inverted fashion (Cu(1) of core-1 is bridged by $\mu_{1,1}$ -N₃ to Cu(2a)* (* symmetry: 2 - x, 1 - y, 1 - z) of core-2 and vice versa) to constitute an eight-member ring. The $Cu(1) \cdots Cu(2)$ distance is 3.13 Å and is similar to reported azido bridged (end-on) dicopper complexes [13] but shorter than oxobridged (Cu–O–Cu) phenolato compounds [7a]. In the single azido bridged (Cu(1)-{ $\mu_{1,1}$ -N₃}-Cu(2 a)^{*}) (* symmetry: 2 - x, 1 - y, 1 - z) dinuclear copper(II) unit the Cu···Cu separation is 3.59(2) Å and is longer than the double azido bridged dicopper unit.

There are three types of (azido) N_3 -groups present in the tetranuclear copper(II) unit: two N₃-units bridge two Cu(II)-centres in the dimeric core; one N₃-function serves to bridge two dimer cores and the last N₃-unit coordinates as a monodentate donor with one of the two copper centres in the dimer. Other N-donor centres are N(imidazole) and N(azo) from the chelated HaaiMe. Out of them, the N(azo) requires considerably more room than the other N-donors [23]. There are at least two steric reasons for this. First, the N(azo) belongs to an exocyclic N=N along with a pendant aryl group; thus the van der Waals repulsion will be greater than N(imidazole). Second, the N(azido) has larger s-character compared to N(azo) and thus N(azo) is more space demanding. The Cu-N(azo) distances are the longest in the series and are Cu(1)-N(8), 2.639(1) and Cu(2)-N(4), 2.632(3) A. However, the Cu-N(azo) distances are less than the sum of the van der Waals radii of Cu(II) and N(azo) [24]. This implies a covalent interaction of N(azo) and Cu(II). Cu(II) has some preference to bind to N(imidazole) [25] compared to N(azo) and is shortened by 0.6 Å. The azido bond lengths lie in the range 1.12–1.21 Å. The azo N=N distances in the two chelated HaaiMe of the dimer are N(3)-N(4), 1.260(3) and N(7)-N(8), 1.243(4) A, which are near to the free ligand value (1.250(1) Å) [26].

2.4. Magnetic study

The variable temperature magnetic susceptibility data for complex **3a** was recorded between 300 and 2 K. A plot of $\chi_M T$ versus T for the four copper(II) ions is shown in Fig. 2. At 300 K, the $\chi_M T$ value is 1.64 cm³ mol⁻¹ K, which

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is close to that expected for four uncoupled spins, with g = 2.09. The value increases slightly on lowering the temperature and reaches a maximum $(1.83 \text{ cm}^3 \text{ mol}^{-1} \text{ K})$ at 22 K. Below this temperature $\chi_M T$ decreases to a value of $1.38 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. The shape of this curve indicates dominant ferromagnetic coupling until 22 K and below this temperature $\chi_{\rm M}T$ decreases from 1.8 to 1.4 cm³ mol⁻¹ K, which is the signature of antiferromagnetic exchange and/ or the presence of the ZFS of the ground state. To analyze the magnetic pathways it is necessary to schematize them as is shown in Fig. 3. This scheme matches with the structure that, as indicated above, can be considered as a dimer of dimers. The J_1 corresponds to the double end-on azido bridges with an equatorial-equatorial (short-short) coordination mode, whereas J_2 corresponds to the single end-on azido bridge, but in equatorial-axial (short-long) coordination mode. Thus, considering these two different J values, the analysis of the experimental susceptibility values has been performed using the following expression:



Fig. 2. Plot of the $\chi_M T$ vs. *T* data for complex **3a**. Solid line represents the best fit (see text).



Fig. 3. Magnetic interaction pathways J_1 and J_2 between the different copper(II) centres.

$$\chi_{\rm M} = Ng^2\beta^2/KT[A/B],\tag{1}$$

where $A = [30\exp(-E_1/kT) + 6\exp(-E_2/kT) + 6\exp(-E_3/kT) + 6\exp(-E_4/kT)], B = 5[\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)].$

 E_n values can be obtained using the Kambe method from the Hamiltonian:

$$\begin{split} H &= -J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - J_2(S_1 \cdot S_3 + S_2 \cdot S_4) \\ E_1 &= (-J_1 - J_2)/2, \quad E_2 = (-J_1 + J_2)/2, \\ E_3 &= (J_1 + J_2)/2, \quad E_4 = (J_1 - J_2)/2, \\ E_5 &= (J_1 + J_2)/2 + (J_1^2 + J_2^2 - J_1J_2)^{1/2}, \\ E_6 &= (J_1 + J_2)/2 - (J_1^2 + J_2^2 - J_1J_2)^{1/2} \end{split}$$

where J_i parameters correspond to those given in Fig. 4. The best fit parameters found are: $J_1 = +25.3 \text{ cm}^{-1}$, $J_2 = -4.7 \text{ cm}^{-1}$, g = 2.07 and $R = 1.6 \times 10^{-4}$, where $R = \sum [(\chi_M T)_{exp} - (\chi_M T)_{cal}]^2 / \sum (\chi_M T)_{exp}^2$. Attempts to fit the experimental data introducing D, zJ' or θ parameters in the expression (1) did not improve the R factor.

The values of the superexchange parameters are $J_1 = +25.3 \text{ cm}^{-1}$ and $J_2 = -4.7 \text{ cm}^{-1}$ which are typical for such Cu(II) complexes with these structural features. The bonding pattern of Cu-(N₃)-Cu is unique in this example, having one single end-on and double end-on azide bridging, and is different from so far reported endon azido bridged Cu(II) complexes (Table 2). Indeed, for the equatorial-equatorial coordination mode (such as in the J_1 pathway), the magnetic behavior of copper-azide bridged complexes in end-on mode is well-known [28–35] and the general trends of their magnetic properties are well-correlated to the structural parameters of the bridge (mainly Cu-Nazide-Cu angle). Currently, the end-on or $(\mu_{1,1})$ double bridges are usually associated with ferromagnetic behavior [5], although for angles out of the range 96–104° the interaction can be antiferromagnetic [27,36]. However, for azido anions bridging in an end-on fashion at the axial-equatorial position (such in the J_2 case, Fig. 3), the reported J values are always small and they can be ferromagnetic or antiferromagnetic [37-42], depending on the Cu–N distance and the τ parameter ($\tau = 0$ for square pyramidal or elongated octahedral geometries and



Fig. 4. ORTEP view of $6a \cdot C_3H_8O_2$ showing the metal environment and the atom labelling.

Selected structural and magnetic data of some single- and double end-on azido bridged Cu(II) complexes

Complex ^a	Cu–N (Å)	Cu–N–Cu (°)	$J({ m cm}^{-1})$	Ref.
Double end-on azido bridged Cu(II) complexes				
$[Cu_2(OBISDIEN)(\mu_2-N_3)_2(N_3)_2]$	1.990, 2.043	105.5, 101.6	70	[28]
$[Cu_2(t-Bupy)4(\mu_2-N_3)_2](ClO_4)_2$	1.99	100.5	105	[29]
$[Cu_2(tbz)_2(\mu_2-N_3)_2(N_3)_2] \cdot 2CH_3OH$	2.059, 1.97	104.7	23	[31]
$[Cu_2(DMPTD)(\mu_2-N_3)_2(N_3)_2]$	1.995, 2.043	98.3, 101.9	85	[36]
$[Cu_2(\mu_{1,1}N_3)_2(4-Etpy)_4(\mu-NO_3)_2]$	1.996, 2.004	98.3	230	[11b]
$[Cu_2(\mu_{1,1}N_3)_2(3-ampy)_4(\mu-NO_3)_2] \cdot C_2H_5OH$	2.000, 2.006	97.5	223	
$[Cu_3(\mu_{1,1}N_3)_4(Meinic)_2(N_3)_2(DMF)_2]$	1.998, 2.012	100.8, 99.2	47.3	
$[Cu(L^1)(N_3)]_2$	2.215, 2.174	90.93	1.03	[33]
$[Cu_4(bpm)_2(N_3)_8]_n$	2.002, 1.998	101.4	11.7	[34]
	2.023, 2.010	102.3		
$[Cu(4-Etpy)(N_3)_2]$	1.970, 1.979	103.0	weak ferro	[11c]
$[Cu_4(L^2)(\mu_2\text{-}N_3)_4](PF_6)_4$	2.012, 1.996	98.1, 96.6	94	[35]
Single end-on azido bridged Cu(II) complexes				
$[Cu_2(terpy)_2 - \mu - (N_3)_4 Cu_2 - \mu - N_3)_2(N_3)_2]$	1.943, 2.374	107.11	-100	[42a]
$Cu_3(SE)_2(N_3)_4(DMF)_2$	2.001, 2.042	102.33	32.6	[42b]
$[Cu_2(\mu - oxen)(\mu_{1,1} - N_3)_2(Br)]_n$	1.98, 1.95	112.5	-85.7	[42c]
$[Cu_4(\mu-\text{oxen})_2(\mu_{1,1}-N_3)_2(\mu-1,3-N_3)]_n(ClO_4)_n$	1.98, 1.98	111.8		[4]
	2.41, 1.95	97.3		
$[Cu_2(hppz)_2(N_3)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$	2.28, 2.01	130.0	-11.5	[42d]
$[Cu_2(L^3)_2(N_3)_2(\mu_{1,1}-N_3)(\mu_{1,3}-N_3)]_n$	2.34, 1.99	116.6	14.1	[42e]
$[Cu_2(Me-L^4)(\mu_{1,1}-N_3)_4]_n$	2.30, 1.97	110.9		
$[Cu(L^5)(N_3)(\mu_{1,1}-N_3)]_n$	2.42, 1.96	113.6	-2.2	[42f]
$[Cu(L^6)(N_3)(\mu_{1,1}-N_3)]_n$	2.60, 1.95	107.1	-3.7	
Single- and double end-on azido bridged, together, in	n compound 1			
Compound 3a	1.973, 2.017	104.7, 100.6	25.3	this work
	2.051, 1.961	106.59	-4.7	

^a OBISDIEN = 1,13-dioxa-4,7,10,16,19,23-hexaazacyclotetracosane; *t*-bupy = 4-*tert*-butylpyridine; (tbz = bis(2-benzimidazolyl)propane; DMPDT = 2,5-bis-((pyridylmethyl)thio)thiadiazole; 4-Etpy = 4-ethylpyridine; 3-ampy = 3-aminopyridine; Meinic = methylisonicotinate; HL¹ = 1-(2-hydroxyben-zyl)-1,5-diazacicloctane; bpm = bis(pyrazol-1-yl)methane; L² = 1,2,4,5-tetrakis-(1,4,7-triazacyclonon-1-ylmethyl)benzene, terpy = 2,2':6,2''-terpyridine; SE = result from the condensation of *N*,*N*-dimethylethylenediamine with salicylaldehyde; H₂oxen = *N*,*N*'-bis(2-aminoethyl)oxamide; hppz = homopiperazine; L³ = 2-(pyrazol-1-yl-methyl)pyridine; Me-L⁴ = 2-(3-methylpyrazol-1-yl-methyl)pyridine. L⁵ and L⁶ are obtained from the condensation of 2-pyridylaldehyde with aniline and *p*-chloroaniline, respectively.

 $\tau = 1$ for trigonal bipyramidal geometry). Thus, the J_2 value of -4.7 cm^{-1} (small for copper(II) ions), can be unequivocally assigned to the monobridge azido ligand (equatorial-axial). The two *J* values found in **3a** match with those shown in Table 2.

2.4.1. Reaction of excess ligand with $[Cu(RaaiR')(N_3)_2]_4$

To a 2-methoxy-ethanol solution of the tetranuclear complex, an excess of the ligand (the same ligand as is present in the tetranuclear copper(II) complex) was added and stirred for a few minutes. Upon addition of water to this solution a brown product was separated. It was then purified by recrystallisation from the mixture of methanol and 2-methoxy ethanol (1/1 v/v). Infrared spectra of the complex show a sharp single band at an average of 2045 cm^{-1} . This supports the presence of terminal N₃bonding. Moderately intense stretchings at 1585-1595 and $1440-1450 \text{ cm}^{-1}$ are referred to v(C=N) and v(N=N), respectively. These complexes are non-conducting and sufficiently soluble in common organic solvents like chloroform, dichloromethane and acetonitrile. The UV-Vis spectra are recorded in acetonitrile solution and show weak absorptions at 706-730 and 570-580 nm. The structural confirmation has been carried out in one case by a single crystal X-ray structure study and is given below in detail. Room temperature (298 K) magnetic data of mononuclear complexes **5** and **6** show the typical values of $\chi_{\rm M}T$ for one unpaired electron (d⁹), around 0.4 cm³ mol⁻¹ K.

2.4.2. $Cu(HaaiEt)_2(N_3)_2 \cdot C_3H_8O_2$ (**6a** $\cdot C_3H_8O_2$)

Crystals are obtained on slow evaporation of a mixture of 2-methoxy ethanol and a methanol solution of [Cu(Haa $iEt_{2}(N_{3})_{2}$ and HaaiEt (in excess). An ORTEP view of $Cu(HaaiEt)_2(N_3)_2 \cdot C_3H_8O_2$ is shown in Fig. 4. Selected bond lengths and angles are given in Table 3. In the discrete molecule, copper(II) is surrounded by two ligands and two azido groups. The ligand serves as an unsymmetric N,N'-chelating agent (N refers to imidazole-N and N' refers to azo-N donor centres) and two ligands chelate in a manner to give cis-N,N and trans-N',N' arrangements. Two N_3^- coordinate in a *cis*-fashion around Cu(II). Thus, the coordination sequence of azides, imidazole-N(N) and azo-N(N') describe a *cis-cis-trans* stereochemical orientation. The geometry of the copper ion is an axially elongated octahedron; the equatorial plane is formed by two imidazole-N (each from an individual ligand) and two azido-N

Table 3 Bond distances (Å) and bond angles (°) of $Cu(HaaiEt)_2(N_3)_2 \cdot C_3H_8O_2$ (**6a** · C_2H_2O_2)

(04 0311802)			
Cu(1)–N(1)	2.003(3)	N(1)-Cu(1)-N(12)	70.28(10)
Cu(1)-N(5)	2.018(3)	N(2)-Cu(1)-N(13)	105.40(13)
Cu(1)-N(12)	2.541(3)	N(5)-Cu(1)-N(7)	90.13(14)
Cu(1)–N(13)	2.569(3)	N(5)-Cu(1)-N(8)	70.84 (12)
Cu(1)–N(2)	1.985(4)	N(5)-Cu(1)-N(12)	88.04 (12)
Cu(1)–N(7)	1.994(3)	N(5)-Cu(1)-N(13)	69.60 (12)
N(1)-C(17)	1.319(5)	N(7)-Cu(1)-N(12)	106.21(12)
N(11)-C(17)	1.396(4)	N(7)-Cu(1)-N(13)	90.48(13)
N(11)–N(12)	1.264(4)	N(12)-Cu(1)-N(13)	152.30(10)
N(13)–N(14)	1.269(5)	N(1)-Cu(1)-N(12)	70.28(10)
N(2)–N(3)	1.201(6)	N(1)-Cu(1)-N(13)	93.35(11)
N(3)–N(4)	1.153(6)	Cu(1)-N(1)-C(17)	119.5(2)
N(7)–N(8)	1.164(6)	Cu(1)-N(2)-N(3)	120.0(3)
N(8)-N(9)	1.159(6)	N(2)-N(3)-N(4)	177.9(5)
N(5)–C(7)	1.326(5)	Cu(1)-N(5)-C(7)	119.0(3)
N(14)-C(7)	1.383(5)	N(1)-Cu1-N2	91.00(13)
		N1-Cu(1)-N(7)	176.16(14)
		N(2)-Cu(1)-N(5)	174.63(15)
		N(2)-Cu(1)-N(7)	87.90(15)
		Cu(1)-N(12)-N(11)	111.6(2)

donor centres. The two axial positions are occupied by two azo-N donor centres of two HaaiEt. The N–Cu–N bond angles subtended by the chelating ligands are N(1)–Cu–N(12), 70.28(10)° and N(5)–Cu–N(13), 69.60(12)° which are close to the precursor tetranuclear copper(II) compound. The arylazoimidazole moiety is almost planar with a deviation from the least square plane <0.04 Å. The chelate rings constitute good planes (mean deviation ~0.03 Å). The pendant aryl ring makes small a dihedral angle with the chelate plane and lie in the range 7–8°. The proposed molecular planes in the octahedral geometry are found to be heavily distorted in this structure. The distortion in CuN₆ coordination is supported from the bond parameters of the structures (Table 3).

There are three types of N-donor centres: N(imidazole), N(azo) and N(azido). Usually Cu-N(azo) distances are longer than the other distances and lie in the range of 2.6–2.7 Å. The reasons of more space of N(azo) have been accounted for earlier (see above) [23-25]. The structural distortion is not only of electronic origin (Jahn-Teller distortion for d^9 , Cu(II)) but also arises from the steric effect of N-donor centres. The lowering in overall symmetry is manifested by the elongation of axial bonds and the two N(azo) donor centres occupy two axial positions. There is a small difference (~ 0.01 Å) between two Cu–N(imidazole) distances [Cu(1)–N(1), 2.003(3); Cu(1)–N(5), 2.018(3) Å]. The sum of the equatorial bond angles (plane is constituted by two imidazole-N and two azido-N donor centres) at Cu is 360.31°. It shows that the metal ion is essentially in the mean plane. A significant deviation from the *trans* angle is observed for the two axial N-donors, more than that of the equatorial N-donors in the chelated fragment Cu(HaaiEt). In the equatorial plane the trans angles are $>170^{\circ}$ [N(1)–Cu(1)–N(7), 176.16(14)°; N(2)–Cu(1)–N(5), 174.63(15)°]. The axial $\angle N$ -Cu-N is >150° [N(12)-Cu(1)- N(13), 152.30(10)°]. The large deviation (\sim 35°) from the *trans* angle (180°) is undoubtedly from the combined contribution of short chelate angle, lifting of the inherent degeneracy of the d⁹ configuration and the steric requirement of azo-N centres. The azido bond lengths and angles

3. Experimental

3.1. Materials

 $Cu(OAc)_2 \cdot H_2O$, NaN₃ were purchased from Sisco Research Lab, India, and 1-alkyl-2-arylazoimdazoles (RaaiR') were prepared following the literature procedures [20]. All other chemicals and solvents were analytical reagent grade. Solvents were used after drying. For spectral studies solvents of spectroscopic grade were purchased from Lancaster, UK. The reaction conditions have been set up following the procedure of synthesis of [Mn-(MeaaiEt)(N₃)₂]_n [14].

are within the range for reported data [9-13]. The azo, N=N, distances lie between 1.26–1.27 Å which is longer

than the free ligand value (1.250(1) Å) [26].

Caution! Azido complexes of transition metal ions containing organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

3.2. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 CHNO/S elemental analyzer. Copper analyses were carried out by iodometric titration [43]. Spectroscopic measurements were carried out using the following instruments: UV-Vis spectra, reflectance spectra, JASCO UV-Vis/NIR model V-570; IR spectra (KBr disk, 4000-200 cm⁻¹), JASCO FT-IR model 420. The room temperature magnetic moment was measured using a vibrating sample PAR-155 magnetometer at 298 K. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model using ca. 10^{-3} M solutions in MeOH. The magnetic susceptibility of a powdered sample was measured using a SQUID Magnetometer in the temperature range 300-2 K at an applied field of 0.1 T. The contribution of the sample holder was determined separately in the same temperature range and field. Diamagnetic corrections were estimated from Pascal's constants. The magnetic susceptibility was fitted by least square techniques.

3.3. Syntheses

3.3.1. $[Cu(HaaiMe)(N_3)_2]_4$ (3a)

A solution of 1-methyl-2-(phenylazo)imidazole (HaaiMe) (0.045 g, 0.24 mmol) in methanol (10 ml) was added dropwise to a stirred solution of $Cu(OAc)_2 \cdot H_2O$ (0.05 g, 0.25 mmol per copper) in MeOH (10 ml) at 298 K. The greenish brown solution was stirred for 15 min. NaN₃ (0.033 g, 0.51 mmol) in MeOH (10 ml) was

added to this solution. The colour changed from greenish brown to red brown. The solution was filtered and left undisturbed for a few days. The dark brown crystalline compounds were collected, washed with aqueous methanol (1:1, v/v) and finally with ether. It was dried in vacuo. Yield was 0.063 g (74%). The microanalytical data of the two complexes is as follows, $[Cu(HaaiMe)(N_3)_2]_4$ (3a): Anal. Calc. for C40H40N40Cu4: C, 35.97; H, 2.99; N, 41.97; Cu, 19.05. Found: C, 35.86; H, 3.05; N, 41.84; Cu, 18.91%. $[Cu(MeaaiMe)(N_3)_2]_4$ (3b) (yield, 65%). Anal. Calc. for C44H48N40Cu4: C, 37.98; H, 3.45; N, 40.28; Cu, 18.28. Found: C, 37.89; H, 3.39; N, 40.37; Cu, 18.14%. [Cu(HaaiEt)(N3)2]4 (4a) (yield, 67%). Anal. Calc. for C44H48N40Cu4: C, 37.98; H, 3.45; N, 40.28; Cu, 18.28. Found: C, 37.92; H, 3.51; N, 40.33; Cu, 18.17%. $[Cu(MeaaiEt)(N_3)_2]_4$ (4b) (yield, 72%). Anal. Calc. for C₄₈H₅₆N₄₀Cu₄: C, 39.83; H, 3.87; N, 38.73; Cu, 17.57. Found: C, 39.89; H, 3.81; N, 38.68; Cu, 17.45%.

3.3.2. Reaction of HaaiMe with $[Cu(HaaiMe)(N_3)_2]_4$

To a well-stirred suspension of $[Cu(HaaiMe)(N_3)_2]_4$ (3a) (0.1 g, 0.30 mmol) in 2-methoxy ethanol (5 ml), a small excess to one equivalent (with reference to per copper atom) of HaaiMe (0.60 g, 0.32 mmol) in methanol (10 ml) was added and stirred continuously for 30 min. By this time the solution colour changed to brown violet. It was then filtered through a G-4 crucible, to reject any residue, and left undisturbed for slow evaporation. Dark coloured crystals appeared after a week. These were then filtered, washed with cold methanol and dried in vacuo over CaCl₂. Yield was 0.09 g (58%). [Cu(HaaiMe)₂(N₃)₂] (5a): Anal. Calc. for C₂₀H₂₀N₁₄Cu: C, 35.97; H, 2.99; N, 41.97; Cu, 19.05. Found: C, 35.86; H, 3.05; N, 41.84; Cu, 18.91%.

 $[Cu(MeaaiMe)_2(N_3)_2]$ (5b) (yield, 55%). Anal. Calc. for C₂₂H₂₄N₁₄Cu: C, 37.98; H, 3.45; N, 40.28; Cu, 18.28. Found: C, 37.89; H, 3.39; N, 40.37; Cu, 18.14%. [Cu(Haa $iEt_{2}(N_{3})_{2}$ (6a) (yield, 60%). Anal. Calc. for $C_{22}H_{24}N_{14}Cu$: C, 37.98; H, 3.45; N, 40.28; Cu, 18.28. Found: C, 37.92; H, 3.51; N, 40.33; Cu, 18.17%. $[Cu(MeaaiEt)_2(N_3)_2]$ (6b) (yield, 58%). Anal. Calc. for C24H28N14Cu: C, 39.83; H, 3.87; N, 38.73; Cu, 17.57. Found: C, 39.89; H, 3.81; N, 38.68; Cu, 17.45%.

3.4. Crystallographic data collection and refinement of the structure

Good quality and stable to X-ray crystals for both the complexes were collected from slow evaporation of synthetic mixtures in methanol and 2-methoxy ethanol. Data were collected with a Siemens SMART CCD diffractometer using fine focus sealed graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined from least-squares refinement of setting angles of 6529 reflections at 293 K for $[Cu(HaaiMe)(N_3)_2]_4$ (3a) and 7195 reflections for $[Cu(HaaiEt)_2(N_3)_2] \cdot C_3H_8O_2$ (6a) at 294 K. Data were collected with 2θ in the range $4.04 \leq 2\theta \leq 56.54^{\circ}$ (for **3a**) and $2.6 \leq 2\theta \leq 56.6^{\circ}$ (for **6a**).

Table	4
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Summarized crystallographic data for **3a** and $6a \cdot C_3H_8O_2$

Compound	3a	$\pmb{6a}\cdot C_3H_8O_2$
Empirical formula	$C_{40}H_{40}N_{40}Cu_4$	C ₂₅ H ₃₂ N ₁₄ O ₂ Cu
Formula weight	1335.32	624.19
Temperature (K)	293	294
Crystal system	orthorhombic	orthorhombic
Space group	Pbca	Pbca
Crystal size (mm) ³	$0.10\times0.08\times0.05$	$0.15 \times 0.20 \times 0.20$
<i>a</i> (Å)	19.2947(14)	12.5670(7)
$b(\mathbf{A})$	14.9915(11)	15.8577(9)
$c(\dot{A})$	19.2947(14)	31.2045(18)
β (°)	90	90
$V(\text{\AA})^3$	5581.1(7)	6218.5(6)
Z	8	8
λ (Å)	0.71073	0.71073
μ (Mo K α) (mm ⁻¹)	1.576	0.750
D_{calc} (Mg m ⁻³)	1.589	1.134
Refined parameters	379	383
Reflection number total	31 861	35918
Unique reflections	6529	7195
$R_1^{a} [I > 2\sigma(I)]$	0.0444	0.0652
wR_2^{b}	0.0970	0.1322
Goodness-of-fit	0.92	0.83
	1	

^a $R = \sum (|F_o - F_c|) / \sum |F_o|$. ^b $wR = [\sum w(F_o^2 - F_c^2) / \sum w(F_o)^2]^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (0.0462P)^2]$ for **3a** and $w = 1/[\sigma^2(F_o)^2 + (0.0659P)^2]$ for **6a**, where $P = ((F_o)^2 + 2(F_o)^2)/3$.

A summary of the crystallographic data and structure refinement parameters is given in Table 4. Reflection data were recorded using the ω scan technique. Data were corrected for Lorentz polarization effects and for linear decay using the SAINT program. Semi-empirical absorption corrections based on ψ -scans were applied. The structure was solved by direct methods using SHELXS-97 [44,45] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual maxima and minima were 0.396 and -0.206 for **3a** and 0.313 and -0.230 for 6a.

4. Conclusion

In this research we demonstrate the synthesis of tetranuclear $[Cu(RaaiR')(N_3)_2]_4$ complexes from the reaction of $Cu(OAc)_2 \cdot H_2O$, RaaiR' and NaN₃ in a 1:1:2 mole ratio. Addition of RaaR' (a slight excess of one equivalent) to a 2-methoxy ethanol solution of the tetranuclear compound has degraded it to a mono-copper compound of composition, $[Cu(RaaiR')_2(N_3)_2]$. In each case, the structural confirmation has been done by X-ray diffraction studies. The tetranuclear arrangement has been achieved by end-on sharing of N₃-groups in the dimers in which six-coordinated CuN₆ and five-coordinated CuN₅ units are associated via two end-on-N₃ bridging groups. IR spectra also distinguish the bonding pattern. Variable temperature magnetic susceptibility measurement (300-2 K) shows both anti- and ferromagnetic interactions for $[Cu(HaaiMe)(N_3)_2]_4$.

Acknowledgements

Financial support from the Council of Scientific and Industrial Research, and Department of Science and Technology, New Delhi are gratefully acknowledged. C.S. also acknowledges UGC for providing him a Visiting Associateship to I.I.Sc., Bangalore. M.S.F. is also grateful for the grant given by the Spanish Ministerio de Ciencia y Tecnologia (Programa Ramon y Cajal). Our sincere thanks are due to Prof. J. Ribas, Universitat de Barcelona, Spain for his helpful discussion on magnetism of the complexes.

Appendix A. Supplementary material

UV–Vis and infrared spectral data are submitted in Supplementary Table. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 249036 for Cu(HaaiEt)₂(N₃)₂ · C₃H₈O₂ and 249037 for [Cu(HaaiMe)(N₃)₂]₄. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006. 04.007.

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