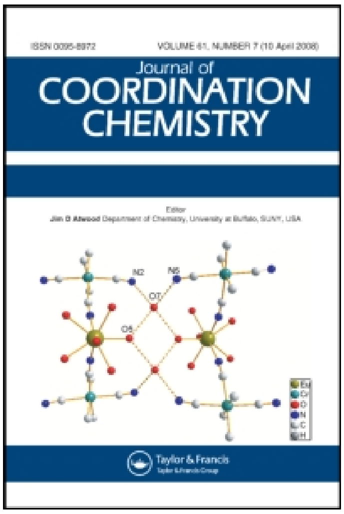

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Synthesis and characterization of mononuclear and dinuclear zinc-arylazoimidazole complexes. single-crystal x-ray structure of $[Zn(HaaiEt)_4](ClO_4)_2$ and $[Zn(HaaiMe)(\mu\text{-}1,1\text{-}N_3)(N_3)]_2$ [HaaiEt = 1-ethyl-2-(phenylazo)imidazole; HaaiMe = 1-methyl-2-(phenylazo)imidazole]

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SYNTHESIS AND CHARACTERIZATION OF MONONUCLEAR AND DINUCLEAR ZINC-ARYLAZOIMIDAZOLE COMPLEXES. SINGLE-CRYSTAL X-RAY STRUCTURE OF $[Zn(HaaiEt)_4](ClO_4)_2$ AND $[Zn(HaaiMe)(\mu\text{-}1,1\text{-}N_3)(N_3)]_2$ [HaaiEt = 1-ETHYL-2-(PHENYLAZO)IMIDAZOLE; HaaiMe = 1-METHYL-2-(PHENYLAZO)IMIDAZOLE]

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(Received 18 November 2003)

$Zn(ClO_4)_2 \cdot 6H_2O$ reacts with 1-alkyl-2-(arylazo)imidazoles [RaaiR′, where R = H (**a**), Me (**b**); R′ = Me (**1**), Et (**2**)] affording orange–yellow $[Zn(RaaiR')_4](ClO_4)_2$ (**3**,**4**) complexes. When excess sodium azide is added to the reaction, orange–red, dimeric azido-complexes of the type $[Zn(RaaiR')(N_3)(\mu\text{-}1,1\text{-}N_3)]_2$ (**5**,**6**) are obtained. Both types of complex were characterized. Structures were confirmed by single-crystal X-ray diffraction studies of $[Zn(HaaiEt)_4](ClO_4)_2$ (**3b**) and $[Zn(HaaiMe)(N_3)(\mu\text{-}1,1\text{-}N_3)]_2$ (**5a**).

Keywords: Arylazoimidazoles; μ-(1,1)-Azido-bridged complex; X-ray structure; Zn(II) complexes

INTRODUCTION

Zinc complexes of heterocyclic N-donor ligands are of current interest because of their biochemical effects [1,2]. In the zinc metalloenzymes, zinc–imidazole bonding is of prime concern. Chemical modification of imidazole and the synthesis of zinc complexes are of special importance in this context [3,4]. For several years we have been engaged in the synthesis of azo-containing imidazole systems (Scheme 1, RaaiH) [5–9]. Exobidentate behaviour has been eliminated by N(1)-alkylation. The transition metal chemistry of 1-alkyl-2-(arylazo)imidazoles (RaaiR′) is known in some detail [5–7]. Non-transition metal complexes of these ligands have received less attention, although some complexes of Group 12 metals are known [10–13]. The ligands act in general as

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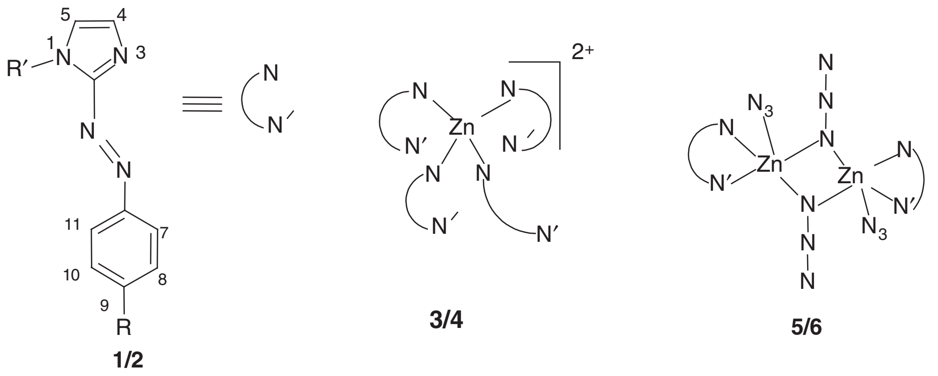

SCHEME 1 RaaiH (R′ = H) and RaaiR′; R = H (**a**), Me (**b**); R′ = Me (**1**/**3**/**5**), Et (**2**/**4**/**6**).

unsymmetric N,N′ chelates. Depending on the nature of the metal and counter ion, they may act as monodentate imidazole-N donors. For example, RaaiR′ binds as a monodentate to Cd(II) when counter ions are Cl^-, ClO_4^- and NO_3^- [13]; in the presence of N_3^- or SCN^- the ligand chelates to Cd(II) [14]. With Hg(II), RaaiR′ binds as an N,N′ chelate in the presence of chloride [12]. Similar observations are noted with $ZnCl_2$ [10]. The N_3^- ion forms bridged polymeric Mn(II) complexes in which the ligand RaaiR′ acts as an end cap. The difference in binding ability of N(imidazole) and N(azo), as is evident from bond length data, leads to interesting magnetic properties for the complexes [9]. In dimeric azido-bridged Co(II)-RaaiR′ complexes the ligand binds to the metal ion as a chelate.

In the presence of ClO_4^- as a counter ion, the ligands act as monodentate imidazole-N donors to Co(II) and Mn(II) [15]. In general, we conclude that in the presence of azide, dinuclear or polynuclear complexes are formed irrespective of the metal ion. This has prompted us to synthesize zinc(II) complexes of RaaiR′ in the presence of N_3^- and ClO_4^- counter ions to verify this position. A binuclear, azido-bridged species $[Zn(RaaiR')(N_3)(\mu\text{-}1,1\text{-}N_3)]_2$ and a tetrahedral complex $[Zn(RaaiR')_4](ClO_4)_2$ have been characterized by spectroscopic techniques and one representative complex of each of the series structurally confirmed by X-ray diffraction studies.

EXPERIMENTAL

Materials

$Zn(ClO_4)_2 \cdot 6H_2O$ was prepared by treatment of zinc carbonate (E. Merck, India) with perchloric acid (E. Merck) followed by slow evaporation on a steam bath, filtration through a fine glass frit and preservation in a desiccator containing conc. sulphuric acid for subsequent use. NaN_3 was purchased from Loba Chemi, Bombay, and 1-alkyl-2-arylazoimidazoles (RaaiR′) were prepared following a literature procedure [5]. All other chemicals and solvents were of reagent grade and used as received.

Physical Measurements

Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 CHNO/S instrument. Spectroscopic measurements were carried out using the following instruments: electronic spectra, Jasco UV–VIS/NIR model V-570; IR spectra (KBr disc, 4000–200 $\mathrm{cm^{-1}}$), Jasco FT-IR model 420. Molar conductances (Λ_M) were measured with a Systronics 304 conductivity meter using *ca.* 10^{-3} M solutions in MeOH. ^{1}H NMR spectra of the complexes were measured with a Bruker 300-MHz spectrometer. Electrochemical measurements were carried out with the use of a computer-controlled EG&G PARC VersaStat model 250 electrochemical instrument using a Pt disc working electrode. The solution was IR compensated and results were collected at 298 K. The reported results are referenced to Ag/AgCl,$\mathrm{Cl^-}$ in acetonitrile and are uncorrected for junction potentials. Estimation of zinc was carried out by a complexometric titration method [16].

Preparation of [Zn(HaaiMe)$_4$](ClO$_4$)$_2$ (3a)

To a methanolic solution (10 $\mathrm{cm^3}$) of HaaiMe (0.074 g, 0.4 mmol), $\mathrm{Zn(ClO_4)_2 \cdot 6H_2O}$ (0.04 g, 0.1 mmol) in the same solvent (10 $\mathrm{cm^3}$) was added dropwise whilst stirring for 30 min. The solution was filtered and left undisturbed for a week. The orange crystalline complex was filtered and washed with water, followed by cold methanol. It was then dried *in vacuo*. The yield was 0.07 g, 65%.

All other complexes were prepared following an identical procedure and the yield varied in the range 65–70%. Microanalytical data for the complexes are as follows: [Zn(HaaiMe)$_4$](ClO$_4$)$_2$ (**3a**): *Anal.* Found: C, 47.50; H, 3.91; N, 22.10; Zn, 6.45. Calc. for $\mathrm{C_{40}H_{40}N_{16}Cl_2O_8Zn}$: C, 47.56; H, 3.96; N, 22.19; Zn, 6.48%. [Zn(HaaiEt)$_4$](ClO$_4$)$_2$ (**3b**): *Anal.* Found: C, 49.48; H, 4.45; N, 21.00; Zn, 6.10. Calc. for $\mathrm{C_{44}H_{48}N_{16}Cl_2O_8Zn}$: C, 49.56; H, 4.50; N, 21.07: Zn, 6.14%. [Zn(MeaaiMe)$_4$](ClO$_4$)$_2$ (**4a**): *Anal.* Found: C, 49.47; H, 4.42; N, 20.98; Zn, 6.45. Calc. for $\mathrm{C_{44}H_{48}N_{16}Cl_2O_8Zn}$: C, 49.56; H, 4.50; N, 21.07; Zn, 6.14%. [Zn(MeaaiEt)$_4$](ClO$_4$)$_2$ (**4b**): *Anal.* Found: C, 51.31; H, 4.85; N, 19.80; Zn, 5.80. Calc. for $\mathrm{C_{48}H_{56}N_{16}Cl_2O_8Zn}$: C, 51.37; H, 4.99; N, 19.98; Zn, 5.83%.

Preparation of Dimeric Azido-bridged Complexes [Zn(HaaiMe)(N$_3$){(μ-1,1)N$_3$}]$_2$ (5a)

HaaiMe (**1a**) (0.02 g, 0.1 mmol) in MeOH (10 $\mathrm{cm^3}$) was added dropwise to a stirred solution of $\mathrm{Zn(ClO_4)_2 \cdot 6H_2O}$ (0.04 g, 0.1 mmol) in MeOH (10 $\mathrm{cm^3}$) at 298 K. The yellow–orange solution was stirred for 20 min. To this stirred solution, $\mathrm{NaN_3}$ (0.013 g, 0.2 mmol) in MeOH (10 $\mathrm{cm^3}$) was added. The colour of the solution changed from yellow–orange to red–orange. The solution was filtered and left undisturbed for a week. Red–orange crystals of compound (**5a**) were obtained. These were washed with water, methanol and ether, and dried *in vacuo*. The yield was 0.05 g (70%). Microanalytical data for the complex are as follows. [Zn(HaaiMe)(N$_3$){(μ-1,1)N$_3$}]$_2$ (**5a**): *Anal.* Found: C, 35.65; H, 2.92; N, 41.62; Zn, 19.43. Calc. for $\mathrm{C_{20}H_{20}N_{20}Zn_2}$: C, 35.77; H, 3.00; N, 41.73; Zn, 19.47%.

All other complexes in this series were prepared by the same procedure. The yield varied from 70 to 75% and microanalytical data for the complexes are as follows. [Zn(HaaiEt)(N$_3$){(μ-1,1)N$_3$}]$_2$ (**6a**): *Anal.* Found: C, 37.11; H, 3.35; N, 39.36; Zn, 18.39. Calc for $\mathrm{C_{22}H_{24}N_{20}Zn_2}$: C, 37.24; H, 3.41; N, 39.49; Zn, 18.43. [Zn(MeaaiMe)(N$_3$){(μ-1,1)N$_3$}]$_2$ (**5b**): *Anal.* Found: C, 37.14; H, 3.38; N, 39.41; Zn, 18.40. Calc. for $\mathrm{C_{22}H_{24}N_{20}Zn_2}$: C, 37.24; H, 3.41; N, 39.49; Zn, 18.43%. [Zn(MeaaiEt)(N$_3$){(μ-1,1)N$_3$}]$_2$ (**6b**): *Anal.* Found: C, 39.10; H, 3.76; N, 38.00; Zn, 17.68. Calc. for $\mathrm{C_{24}H_{28}N_{20}\,Zn_2}$: C, 39.08; H, 3.82; N, 37.99; Zn, 17.73%.

TABLE I Crystallographic data for [Zn(HaaiEt)$_4$](ClO$_4$)$_2$ (**3b**) and [Zn(HaaiMe)(N$_3$){(μ-1,1)N$_3$}]$_2$ (**5a**)

Empirical formula	$C_{44}H_{48}N_{16}Cl_2O_8Zn$	$C_{20}H_{20}N_{20}Zn_2$
Formula weight	1065.27	671.34
Temperature/K	293	293
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
Crystal size/mm	0.22 × 0.20 × 0.15	0.25 × 0.20 × 0.13
Unit cell dimensions		
a/Å	19.6819(14)	8.0651(6)
b/Å	13.0205(9)	16.5830(13)
c/Å	19.2936(14)	10.5005(8)
β/°	91.76	102.3070(10)
V/Å^3	4942.00(6)	1372.10(18)
Z	4	2
λ/Å	0.71073	0.71073
μ(Mo Kα)/mm^{-1}	0.674	1.801
ρ_{calc}/mg m^{-3}	1.432	1.625
Refine parameters	321	190
Reflection number (total)	5627	7971
Reflection number (ind.)	3644	2518
R^a [$I > 2\sigma(I)$]	0.0554	0.0276
$wR_2{}^b$	0.1564	0.0765
Goodness-of-fit	1.03	1.08

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

[b] $wR = [\sum w(F_o^2 - F_c^2)/ \sum wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0891P)^2 + 0.6795P]$ for **3b** and $w = 1/[\sigma^2(F_o^2) + (0.0440P)^2 + 0.1044P]$ for **5a**, where $P = (F_o^2 + 2F_c^2)/3$.

X-ray Diffraction

Data were collected with a Siemens SMART CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K for both **3b** and **5a**. Unit cell parameters were determined from least-squares refinement of setting angles of 3644 and 2518 reflections in the 2θ range 3.8–58.4 and 4.6–56.4° for **3b** and **5a**, respectively. A summary of crystallographic data and structure refinement parameters is given in Table I. Reflection data were recorded using the ω scan technique. Data were corrected for Lorentz polarization effects and for linear decay. Semi-empirical absorption corrections based on ψ-scans were applied. The structures were solved by the heavy atom methods using SHELXS-97 and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using the riding model.

RESULTS AND DISCUSSION

Four 1-alkyl-2-(arylazo)imidazole ligands [Scheme 1, RaaiR′ (**1**, **2**)] were used in the study. They may serve either as unsymmetric, N,N′-bidentate chelates [5–9] or as monodentate imidazole-N donors [13,15] where N and N′ refer to N(imidazole) and N(azo) donor centres, respectively. Reaction of Zn(ClO$_4$)$_2 \cdot$ 6H$_2$O and RaaiR′ in MeOH gave tetrahedral [Zn(RaaiR′)$_4$](ClO$_4$)$_2$ (**3**, **4**) complexes.

The versatility of the azido ligand (N_3^-) is well established [9,17]. Binuclear (μ-1,1) (EO), azido-bridged monochelated [Zn(RaaiR′)(N$_3$){(μ-1,1)N$_3$}]$_2$ (**5**, **6**) complexes were isolated by reaction of Zn(ClO$_4$)$_2 \cdot$ 6H$_2$O and RaaiR′ in MeOH and sodium azide (in MeOH) with a 1 : 1 : 2 mol ratio, respectively. Reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ in excess of RaaiR′ (>5 mol) in the presence of 2 equivalents of NaN_3 also gave **5** and **6**. Complexes **3** and **4** are 1 : 2 electrolytes in MeOH ($\Delta_M = 140 - 170\,\Omega^{-1}\,cm^{-1}\,mol^{-1}$) while complexes **5** and **6** are non-electrolytes. Spectroscopic properties also support the binding picture of the ligands around zinc(II) revealed by the structure analysis.

STRUCTURE DESCRIPTION

*[Zn(HaaiEt)$_4$](ClO$_4$)$_2$ (**3b**)* The structure is shown in Fig. 1. Selected bond parameters are given in Table II. The cationic complex consists of a central zinc atom surrounded by two pairs of HaaiEt ligands, which are symmetry related. Zn sits at the centre of a tetrahedron. Zn–N bond lengths are Zn–N1a, 2.043(2), Zn–N1b, 2.051(2) Å. HaaiEt acts as a monodentate ligand and binds through imidazole-N. The coordination environment about Zn is compressed along the crystallographic *c* axis in such a way that two of the N–Zn–N angles are greater than the tetrahedral angle with values N1a–Zn–N1a*, 127.87(9) and N1b–Zn–N1b*, 125.23(8)°. The remaining N–Zn–N angles are 100.48(9) and 102.84(9)°. The angular distortion may be due to steric crowding caused by the pendant azophenyl groups. N=N bond lengths are N3a–N4a, 1.254(4) and N3b–N4b, 1.243(4) Å and are near to the free ligand value [18,19].

*[Zn(HaaiMe)(N$_3$){(μ-1,1)N$_3$}]$_2$ (**5a**)* A perspective view of the structure is shown in Fig. 2. Selected bond distances and angles are given in Table III. The ZnN_5 coordination sphere around each Zn(II) is a distorted square pyramid as can be seen from the angles subtended at the metal ion. HaaiMe binds in the usual chelating fashion and the bite angle is 71.90(6). The molecule has a centre of symmetry and the bridging parallelogram is constructed by Zn_2N_2 [N(azido)] motifs. The bridge angles are Zn–N(5)–Zn(a), 98.97(7) and N(5)–Zn–N(5a), 81.03(7). Azide (N_3) bridges two zinc centres

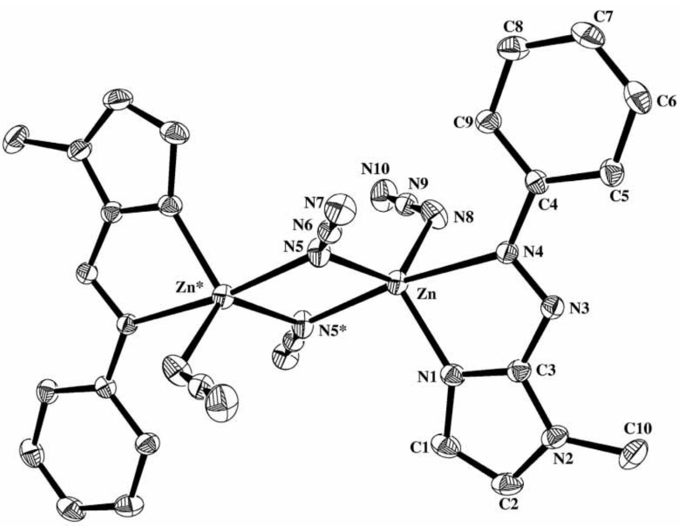

FIGURE 1 Perspective view of [Zn(HaaiEt)$_4$](ClO$_4$)$_2$ (**3b**).

TABLE II Bond distances (Å) and angles (°) for $[Zn(HaaiEt)_4](ClO_4)_2$ (**3b**)

Zn–N(1a)	2.043(2)	N(1a)–Zn–N(1a*)	127.87(13)
Zn–N(1a*)	2.043(2)	N(1a)–Zn –N(1b)	102.84(9)
Zn–N(1b)	2.051(2)	N(1a)–Zn–N(1b*)	100.48(9)
Zn–N(1b*)	2.051(2)	N(1a*)–Zn–N(1b)	100.48(9)
N(3a)–N(4a)	1.254(3)	N(1b)–Zn–N(1b*)	125.23(8)
N(3b)–N(4b)	1.242(3)	N(1a*)–Zn–N(1b*)	102.84(9)
Cl–O(1)	1.381(4)	C(3a)–N(1a)–Zn	129.1(2)
Cl–O(2)	1.417(3)	C(1a)–N(1a)–Zn	125.7(2)
Cl–O(3)	1.395(4)	N(4a)–N(3a)–C(3a)	112.1(2)
Cl–O(4)	1.397(3)	N(3a)–N(4a)–C(4a)	115.0(3)
		C(3b)–N(1b)–Zn	129.62(19)
		C(1b)–N(1b)–Zn	124.0(2)
		N(4b)–N(3b)–C(3b)	112.6(2)
		N(3b)–N(4b)–C(4b)	114.8(3)

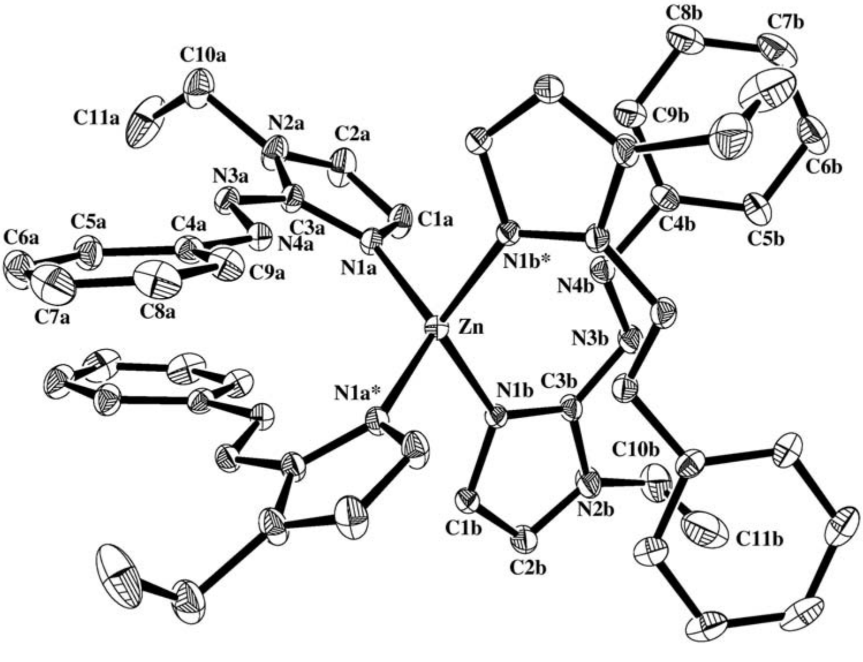

FIGURE 2 X-ray structure of the azido-bridged dimer, $[Zn(HaaiMe)(N_3)\{(\mu\text{-}1,1)N_3\}]_2$ (**5a**).

in a μ-(1,1) fashion. The Zn–N(azo) [Zn–N(4), 2.4468(15) Å] bond length is longer than Zn–N(imidazole) distances [Zn–N(1), 2.0144(17) Å]. The axial Zn–N(azido) [Zn–N(8), 1.9626(18)] is the shortest bond length. The bridged Zn–N(azido) distances are Zn–N(5), 2.0262(17) and Zn–N(5a), 2.1579(18) Å. Distortion of the square plane constituted by Zn, N(4), N(1), N(5), N(5a) is observed and the dihedral angle between the chelate plane [Zn, N(1), C(3), N(3), N(4)] and the bridged parallelogram [Zn, N(5), N(5a), Zn(a)] is 60.99(7). Zn–N(8) is not perpendicular to the square plane. Bond angle data support this proposition: N(4)–Zn–N(8), 86.79(7); N(1)–Zn–N(8), 120.37(8); N(5a)–Zn–N(8), 104.85(8); N(5)–Zn–N(8), 120.59(8). The bridged-N_3 and axial-N_3 bond lengths and angles are as usual [17].

TABLE III Selected bond distances (Å) and angles (°) for [Zn(HaaiMe) $(N_3)\{(\mu\text{-}1,1)N_3\}]_2$ (**5a**)

Zn–N1	2.0144(17)	N1–Zn–N4	71.90(6)
Zn–N4	2.4468(15)	N1–Zn–N5	116.28(7)
Zn–N5	2.0262(17)	N1–Zn–N8	120.37(8)
Zn–N8	1.9626(18)	N1–Zn–N5a	99.95(7)
Zn–N5a	2.1579(18)	N4–Zn–N5	94.78(6)
N1–C3	1.322(3)	N4–Zn–N8	86.79(7)
N3–N4	1.262(2)	N4–Zn–N5a	168.20(6)
N3–C3	1.387(2)	N5–Zn–N8	120.59(8)
N5–N6	1.209(2)	N5–Zn–N5a	81.03(7)
N6–N7	1.139(2)	N5a–Zn–N8	104.85(8)
N8–N9	1.179(3)	Zn–N1–C3	117.09(12)
N9–N10	1.156(3)	N4–N3–C3	111.51(15)
Zn···Zna	3.1820(4)	Zn–N4–N3	11.93(11)
		Zn–N5–N6	126.32(14)
		N1–C3–N3	126.65(17)
		Zn–N5–Zna	98.97(7)
		Zna–N5–N6	132.19(14)
		N5–N6–N7	179.0(2)
		Zn–N8–N9	123.22(16)
		N8–N9–N10	176.4(2)

Spectroscopic Studies

The main vibrational absorption bands were assigned by comparison with data for the free ligand [20]. N=N and C=N vibrations are observed at 1420–1430 and 1590–1600 cm^{-1}, respectively. Complexes **3** and **4** exhibit a very strong absorption at 1105–1085 cm^{-1} with a weak component at 625–630 cm^{-1} due to $\nu(ClO_4)$. Complexes **5** and **6** show a strong doublet at 2095–2098 and 2063–2075 cm^{-1} corresponding to $\nu_{asym}(N_3)$. This reflects the bonding mode of N_3^- as end-on [μ-(1,1)] [21].

Solution electronic spectra of the complexes were recorded in methanol solution in the range 250–900 nm. The complexes give transitions at less than 400 nm corresponding to intramolecular ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) charge transfer. A weak additional band is also observed at 440–460 nm. This may be due to charge transfer between zinc(II) and RaaiR′. $[Zn(RaaiR')_4](ClO_4)_2$ (**3** and **4**) show stronger transitions than azido derivatives **5** and **6**, and this may be due to the distorted tetrahedral geometry of the former complexes as compared to the pyramidal geometry of $[Zn(RaaiR')(N_3)\{(\mu\text{-}1,1)N_3\}]_2$ (**5**, **6**).

CONCLUSIONS

1-Alkyl-2-(arylazo)imidazoles (RaaiR′) are established unsymmetric N(azo), N(imidazole) chelating agents. In the reaction between $Zn(ClO_4)_2$ and an excess of RaaiR′, a tetrakis $[Zn(RaaiR')_4](ClO_4)_2$ compound was isolated and structurally characterized as a tetrahedral Zn(II) system where the ligand acts as a monodentate N(imidazole) donor. However, addition of NaN_3 to the same reaction mixture gave end-on, azido-bridged dimeric zinc complexes in which the ligand shows chelating behaviour. Perhaps azide coordination to Zn(II) provides the requisite acidity and structural formality to the metal centre to force a change in bonding behaviour.

Acknowledgments

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. for $[Zn(HaaiEt)_4](ClO_4)_2$ (**3b**) and $[Zn(HaaiMe)(N_3)\{(\mu\text{-}1,1)N_3\}]_2$ (**5a**), respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1FZ, UK.

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