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Mono- and binuclear cobalt(II)-azido complexes of arylazoimidazole: synthesis, spectral characterization, electrochemistry and crystal structure

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Abstract

Upon setting up proper reaction conditions 1-alkyl-2-(arylazo)imidazoles (RaaiR′ where R = H (**a**), Me (**b**); R′ = Me (**1/3/5**), Et (**2/4/6**) may react with $Co(OAc)_2 \cdot 4H_2O$ and NaN_3 in methanolic solution to give two classes of azido complexes: mononuclear bis-chelated $[Co(RaaiR')_2(N_3)_2]$ (**3**,**4**) and binuclear μ-(1,1) azido bridged mono-chelated $[Co(RaaiR')(\mu\text{-}(1)N_3)(\mu\text{-}(1,1)N_3]_2$ (**5**,**6**) complexes. They are characterized by UV–Vis, IR spectra, room temperature magnetism and they have been structurally confirmed by X-ray diffraction study of $[Co(MeaaiMe)_2(N_3)_2]$ (**3b**) and $[Co\{(\mu\text{-}1)N_3\}(MeaaiMe)]_2$ (**5b**). The mononuclear complex (**3b**) is distorted octahedral whereas the binuclear azide bridged complex (**5b**) has the distorted square pyramidal geometry around the cobalt(II) centre. Redox properties of the complexes are examined by cyclic voltammetry and show a high potential Co(III)/Co(II) couple along with ligand reductions. EHMO calculation and comparison between the two types of complexes explain the spectral and redox properties of the complexes.

Keywords: Arylazoimidazoles; Cobalt(II) complexes; EO azido bridged complexes; X-ray structures

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1. Introduction

Interest in the transition metal coordination chemistry of the azoimine function (–N=N–C=N–) is rapidly expanding in several areas ranging from organometallic chemistry, metal assisted organic transformation, radical chemistry, stabilization of low valent metal oxidation state to DNA labelling and anticancer medicine [1–19]. Incorporation of the arylazo group ($Ar–N^+{\equiv}N$) into backbone of a *N*-heterocycle at the *ortho* position has lead to the synthesis of arylazoheterocycles which have an azoimine function. The activity of the group is dependent on the nature of substituents, number of heteroatoms, and ring size of the heterocycle. The most significant change has been observed on changing the heterocycle ring size [20]. In the scope of our continuous research in this field we have extended our research to design a new series of azoheterocycles in the imidazole backbone. Imidazole and related compounds have been widely used in chemistry and biology due to their appearance as such in biomolecules, metalloproteins [21–23] and their versatility in the production of polymetallic complexes of magneto-chemical interest [24,25]. We have taken a strategy to incorporate an $Ar–N^+{\equiv}N$ imidazole backbone which leads to the synthesis of 2-(arylazo)imidazoles. Bridge forming ability of imidazole has been eliminated upon alkylation and we have synthesized 1-alkyl-2-(arylazo)imidazoles (abbreviated RaaiR′) [26,27]. The present work stems from our continuous interest to explore transition metal chemistry of RaaiR′ [26–33]. Herein we describe mono- and binuclear cobalt(II)-azide complexes of RaaiR′. Synthesis, structures and electrochemistry are described herewith.

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2. Experimental

2.1. Materials

$Co(OAc)_2\cdot 4H_2O$ and NaN_3 were purchased from Loba chemicals, Bombay, India and 1-alkyl-2-arylazoimdazoles (RaaiR′) were prepared following the literature procedures [31]. All other chemicals, solvents are reagent grade as received. Solvents are used after drying.

2.2. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 CHNO/S elemental analyzer. Spectroscopic measurements were carried out using the following instruments: UV–Vis spectra, JASCO UV–Vis–NIR model V-570; IR spectra (KBr disk, 4000–200 cm^{-1}), JASCO FT-IR model 420 spectrophotometers. Room temperature magnetic moment was measured using a Vibronic sample magnetometer. Molar conductances (Λ_M) were measured in a Systronics conductivity meter 304 model using ca. 10^{-3} M solutions in MeOH. Electrochemical measurements were carried out with the use of a computer controlled EG & G PARC VersaStat model 250 electrochemical instrument using a Pt-disk working electrode in acetonitrile at 298 K. The solution was IR compensated and the results were collected at 298 K. The reported results are referenced to a Ag/AgCl, Cl^- electrode in the presence of $[^nBu_4N][ClO_4]$ as supporting electyrolyte and are uncorrected for junction potential. Estimation of cobalt was carried out by the complexometric titration method [34].

2.3. Preparation of mononuclear azido complexes, $Co(MeaaiMe)_2(N_3)_2$ (3b)

1-Methyl-2-(*p*-tolylazo)imidazole (MeaaiMe) (0.1 g, 0.50 mmol) in MeOH (10 ml) was added dropwise to a stirred solution of $Co(OAc)_2\cdot 4H_2O$ (0.062 g, 0.25 mmol) in MeOH (10 ml) at 298 K. The brown solution was stirred for 15 min followed by the addition of NaN_3 (0.03 g, 0.50 mmol) in MeOH (10 ml). The brown color of the solution became intensified. The solution was filtered and then left undisturbed for a week. A dark brown crystal was obtained. It was washed with water, methanol and ether. Finally, it was dried in vacuo. Yield was 0.108 g, (80%). The microanalytical data of the complex is as follows, $[Co(MeaaiMe)_2(N_3)_2]$ (**3b**): *Anal.* Found: C, 48.81; H, 4.57; N, 36.01; Co, 11.25. Calc. for $C_{22}H_{24}N_{14}Co$: C, 48.62; H, 4.42; N, 36.10; Co, 10.85%.

All other complexes were prepared by the same procedure. In all cases, crystalline products were obtained. The yield varied from 75–80% and microanalytical data of the complexes are as follows. $[Co(HaaiMe)_2(N_3)_2]$ (**3a**): *Anal.* Found: C, 46.75; H, 4.01; N, 37.99; Co, 11.04. Calc. for $C_{20}H_{20}N_{14}Co$: C, 46.60; H, 3.88; N, 38.06; Co, 11.44%. $[Co(HaaiEt)_2(N_3)_2]$(**4a**) *Anal.* Found: C, 48.71; H, 4.20; N, 36.08; Co, 11.12. Calc. for $C_{22}H_{24}N_{14}Co$: C, 48.62; H, 4.42; N, 36.10; Co, 10.85%. $[Co(MeaaiEt)_2(N_3)_2]$ (**4b**): *Anal.* Found: C, 50.38; H, 2.56; N, 34.39; Co, 10.19. Calc. For $C_{24}H_{28}N_{14}Co$: C, 50.44; H, 2.45; N, 34.32; Co, 10.32%.

2.4. Preparation of binuclear azido bridge complexes, $[Co(MeaaiMe)\{\mu\text{-}(1)N_3\}\{\mu\text{-}(1,1)N_3\}]_2$ (5b)

NaN_3 (0.065 g, 1 mmol) in MeOH (10 ml) was added dropwise to a stirred solution of $Co(OAc)_2\cdot 4H_2O$ (0.062 g, 0.25 mmol) in MeOH (10 ml) at 298 K. The brown solution was stirred for 15 min and MeaaiMe (**1b**) (0.05 g, 0.25 mmol) in MeOH (10 ml) was added. The color of the solution became dark brown. The solution was filtered and then left undisturbed for a week. The dark brown crystal of compound (**5b**) was obtained. It was then washed with water, methanol and ether. Finally, it was dried in vacuo. Yield was 0.128 g, (75%). The microanalytical data of the complex is as follows, $[Co(MeaaiMe)\{\mu\text{-}(1)N_3\}\{\mu\text{-}(1,1)N_3\}]_2$ (**5b**): *Anal.* Found: C, 38.37; H, 3.56; N, 40.89; Co, 17.07. Calc. for $C_{22}H_{24}N_{20}Co_2$: C, 38.49; H, 3.49; N, 40.82; Co, 17.18%.

All other complexes in this series were prepared by the same procedure. The yield was varied from 70–75% and microanalytical data of the complexes are as follows. $[Co(HaaiMe)\{\mu\text{-}(1)N_3\}\{\mu\text{-}(1,1)N_3\}]_2$ (**5a**): *Anal.* Found: C, 36.53; H, 3.10; N, 42.65; Co, 17.12. Calc. for $C_{20}H_{20}N_{20}Co_2$: C, 36.48; H, 3.04; N, 42.56; Co, 17.12%. $[Co(HaaiEt)\{\mu\text{-}(1)N_3\}\{\mu\text{-}(1,1)N_3\}]_2$ (**6a**): *Anal.* Found: C, 38.63; H, 3.54; N, 41.02; Co, 17.13. Calc. for $C_{22}H_{24}N_{20}Co_2$: C, 38.49; H, 3.49; N, 40.82; Co, 17.18%. $[Co(MeaaiEt)\{\mu\text{-}(1)N_3\}\{\mu\text{-}(1,1)N_3\}]_2$ (**6b**): *Anal.* Found: C, 40.45; H, 4.01; N, 39.38; Co, 16.72. Calc. For $C_{24}H_{28}N_{20}Co_2$: C, 40.34; H, 3.92; N, 39.22; Co, 16.51%.

2.5. X-ray crystal structure analyses

Data were collected with a Siemens SMART CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K for **3b** and 295 K for **5b**. Unit cell parameters were determined from least-squares refinement of setting angles of 2848 reflections for **3b** and 1956 reflections for **5b** with 2θ in the range $4.2 \leq 2\theta \leq 55°$ and $4.4 \leq 2\theta \leq 56.6°$, respectively. A summary of the crystallographic data and structure refinement parameters are given in Table 1. 15 955 reflections were collected in the range $4.2 \leq 2\theta \leq 55°$ with 5744 unique reflections for **3b** and 8548 reflections were collected $4.4 \leq 2\theta \leq 56.6°$ with 3257 unique reflections for **5b**. Data were corrected for Lorentz polarization effects and for linear decay. Empirical absorption

Table 1
Summarised crystallographic data for [Co(MeaaiMe)$_2$(N$_3$)$_2$] (**3b**) and [Co(MeaaiMe)(N$_3$)$_2$(1,1-μ)]$_2$] (**5b**)

	[Co(MeaaiMe)$_2$(N$_3$)$_2$] (**3b**)	[Co(N$_3$)$_2$(1,1-μ)(MeaaiMe)]$_2$ (**5b**)
Empirical formula	$C_{22}H_{24}N_{14}Co$	$C_{22}H_{24}N_{20}Co_2$
Formula weight	543.48	686.47
Temperature (K)	293	295
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Crystal size (mm)	0.27 × 0.20 × 0.14	0.25 × 0.20 × 0.13
Unit cell dimensions		
a (Å)	7.5873(5)	7.9633(9)
b (Å)	16.9677(12)	15.4677(17)
c (Å)	19.9773(14)	11.8266(13)
β (°)	100.499(2)	91.55(1)
V (Å)^3	2528.8(3)	1456.2(3)
Z	4	2
λ (Å)	0.71073	0.71073
μ (Mo Kα) (mm^{-1})	0.720	1.192
D_{calc} (Mg m^{-3})	1.428	1.566
Refine parameters	338	199
Total reflections	15 955	8548
Unique reflections	2848	1956
R [a] $[I > 2\sigma(I)]$	0.0370	0.0402
wR_2 [b]	0.0519	0.0989
Goodness-of-fit	0.969	0.907
Δ_{max} (e Å^{-3})	0.589	0.300
Δ_{min} (e Å^{-3})	−0.384	−0.316

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

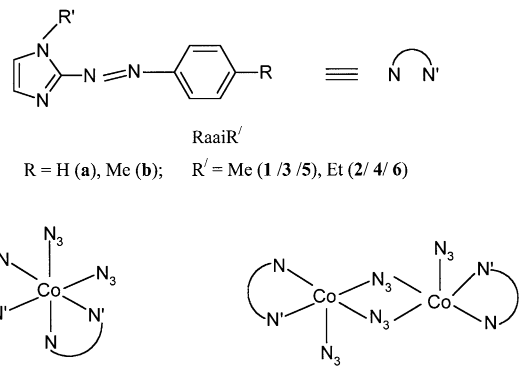
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0055P)^2]$ for **3b** and $w = 1//[\sigma^2(F_o^2) + (0.049P)^2]$ for **5b** where $P = (F_o^2 + 2F_c^2)/3$.

corrections were applied. The structure was solved by 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. All calculations were carried out using SHELXL-97, ORTEP-3 and PLATON-99.

3. Result and discussion

3.1. The ligands and complexes

Two classes of 1-alkyl-2-(arylazo)imidazoles (RaaiR′), total of four have been used as chelating ligands in the present work. They are unsymmetric, N,N'-bidentate chelator where N and N' refer to N(imidazole) and N(azo) donor centers.



RaaiR′

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

3, 4 **5, 6**

The versatility of azido ligand (N$_3$$^-$) is well established. It can act as monodentate μ-(1) [35] and bidentate bridging μ-(1,1)·(EO), μ-(1,3)·(EE), μ-(1,1,1), μ-(1,1,3), alternating μ-(1,1) and μ-(1,3) type [36–41]. Rational control in the construction of mono-/bi-/polynuclear networks is a great challenge in coordination polymers, supramolecules and crystal engineering.

Upon manipulation of reaction condition (solvent and temperature), metal–ligand–azido ratio and sequence of mixing of reactants and reagents these two classes of azido compounds, mononuclear bis-chelated Co(RaaiR′)$_2$(N$_3$)$_2$ (**3**,**4**) and binuclear μ-(1,1)·(EO) azido bridged mono-chelated [Co(RaaiR′)(μ-(1)N$_3$)(μ-(1,1)N$_3$)]$_2$ (**5**,**6**) have been isolated. Bis-chelated mononuclear MX$_2$(RaaiR′)$_2$ (X = halogen), M = Ru, Os) pseudooctahedral complexes can, in principle, exist in five geometrical isomeric forms. The isomers are named *cis–trans–trans* (*ctt*), *trans–trans–trans* (*ttt*), *trans–cis–cis* (*tcc*), *cis–cis–trans* (*cct*) and *cis–cis–cis* (*ccc*) with reference to the sequence of coordination pairs X,X; N,N; N′,N′ respectively. We have established two isomers *tcc* and *ctc* in the case of ruthenium(II) by single crystal X-ray crystallographic study [29] and four isomers (*tcc*, *ctc*, *cct* and ccc) by solution spectroscopic (UV–Vis–NIR and ^{1}H NMR) data [30]. In this case, Co(N$_3$)$_2$(MeaaiMe)$_2$, we find for the first time the *ccc*-isomeric disposition around the metal ion (vide infra).

$$\mathrm{Co(OAc)_2} + 2\mathrm{RaaiR'} + 2\mathrm{NaN_3} \xrightarrow[\text{stir. 298 K}]{\text{MeOH}} \underset{\mathbf{3/4}}{\mathrm{Co(N_3)_2(RaaiR')_2}} + 2\mathrm{NaOAc} \quad (1)$$

$$\mathrm{Co(OAc)_2} + \mathrm{RaaiR'} + \underset{(n>4)}{n\mathrm{NaN_3}} \xrightarrow[\text{298 K}]{\text{MeOH}} \underset{\mathbf{5/6}}{[\mathrm{Co}(\mu-(1)\mathrm{N_3})(\mu-(1,1)\mathrm{N_3})(\mathrm{RaaiR'})]} \quad (2)$$

Bi-azido-bis-chelated Co(N$_3$)$_2$(RaaiR′)$_2$ (**3**,**4**) have been isolated from a reaction where a composition Co(OAc)$_2$:RaaiR′:NaN$_3$ of 1:2:2 (Eq. (1)) is maintained. The complexes **5**,**6** have been prepared mixing Co(OAc)$_2$, RaaiR′ and NaN$_3$ in 1:1:excess (> 4 mole) mole proportion in MeOH (Eq. (2)). Dimers (**5**,**6**) are also isolated from the reaction in which the sequence of addition is $Co(OAc)_2 + NaN_3$ (> 4 mole) followed by 1 mole of RaaiR′. In both cases, the complexes are isolated from the reaction mixture on slow evaporation under ambient conditions. The complexes are non-electrolytes in MeCN. The composition of the complexes was supported by C, H, N data. Metal analyses were carried out by complexometric titration [34].

Table 2
Selected bond distance (Å) and angles (°) for $[Co(MeaaiMe)_2(N_3)_2]$ (**3b**)

Bond distance (Å)		Bond angle (°)	
Co–N11	2.4045(17)	N11–Co–N31	71.40(6)
Co–N31	2.0461(18)	N12–Co–N32	69.88(7)
Co–N12	2.5199(18)	N4–Co–N1	100.33(9)
Co–N32	2.0768(18)	N4–Co–N32	98.71(7)
Co–N1	2.026(2)	N4–Co–N12	81.90(7)
Co–N4	2.0188(17)	N4–Co–N31	145.19(8)
N1–N2	1.169(3)	N4–Co–N11	90.23(7)
N2–N3	1.161(3)	N1–Co–N32	97.97(8)
N4–N5	1.182(3)	N1–Co–N12	167.84(7)
N5–N6	1.157(3)	N1–Co–N31	105.99(8)
N12–N22	1.266(2)	N1–Co–N11	82.49(7)
N11–N21	1.276(2)	N11–Co–N32	170.79(6)
N22–C102	1.385(3)	N11–Co–N12	109.53(6)
C102–N32	1.325(3)	N31–Co–N12	77.16(6)
N21–C101	1.390(3)	N31–Co–N32	99.74(7)
C101–N31	1.316(3)	Co–N4–N5	135.96(17)
		N4–N5–N6	177.2(2)
		Co–N1–N2	134.86(18)
		N1–N2–N3	177.5(3)

3.2. Structure description

3.2.1. $[Co(MeaaiMe)_2(N_3)_2]$ (**3b**)

The molecular structure of $[Co(MeaaiMe)_2(N_3)_2]$ (**3b**) is shown in Fig. 1. Selected bond distances and angles are given in Table 2. The molecule shows distorted octahedral arrangement about Co(II) with *cis*-(N_3),(N_3) *cis*-N(imidazole), N(imidazole) and *cis*-N(azo), N(azo) donor centers and has been named thereafter *cis*–*cis*–*cis* or *ccc*-$[Co(MeaaiMe)_2(N_3)_2]$. The N–Co–N bond angles subtended by the chelating MeaaiMe ligands are N(11)–Co–N(31), 71.3(9)°, N(12)–Co–N(32), 69.8(8)°. The deviation from the ideal 90° for a regular octahedral geometry is a result of steric requirements of the bidentate ligands. Other angles in the chelated motif (Co– [N=N–C = N]) are also deviated in either direction from the regular five-membered ring. The angles around Co(II) in the CoN_6 coordination geometry suggest axial binding of one N_3 group and the other axial position is occupied by imidazole-N (N(31)) from one of the two MeaaiMe ligands. The steric requirement of the N(azo) centers may force them to take position in the equatorial site leading to the *ccc*-configuration. The atomic arrangements Co, N1, N11, N12, N32 (deviation < 0.07 Å) and Co, N4, N11, N31, N32 (deviation < 0.08 Å) and Co, N1, N4, N12, N3 (deviation < 0.02 Å) constitute three planes. The planes are mutually orthogonal extending dihedral angles in the range 85–97°. Two chelating arrangements of atoms Co, N31, C101, N21, N11 (deviation < 0.03 Å) and Co, N12, N22, C102, N32 (deviation < 0.04 Å) constitute excellent planes and make a dihedral angle of 71°. The pendant *p*-tolyl rings are nearly planer with their respective chelate planes and their average dihedral angle is 8°.

There are six unequal Co–N bonds in the CoN_6 sphere to support distorted octahedron geometry. The

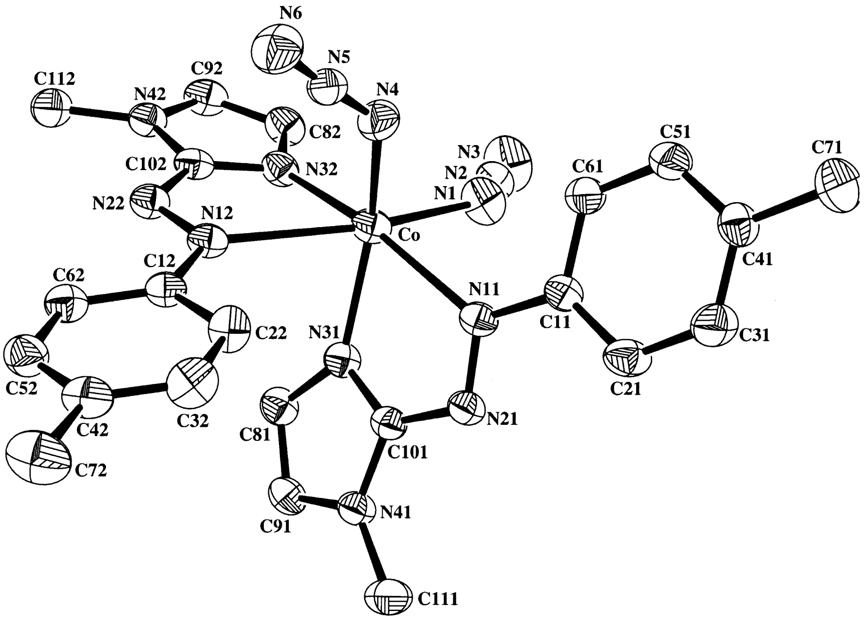


Fig. 1. ORTEP plot of $[Co(MeaaiMe)_2(N_3)_2]$ (**3b**).

Co–N(azido) [Co–N(1), 2.026(4), Co–N(4), 2.019(1) Å] bonds are shortest in this series and are comparable with literature values [42]. The Co–N(azo) [Co–N(11), 2.404(5), Co–N(12), 2.519(9) Å] bonds are the longest in the Co–N family which are reasonably less than the sum of the van der Waal's radii of participating atoms [43] and accounts for covalent interaction. The steric requirement of the bidentate ligands and short chelate rings may be manifested by elongation of the Co–N(azo) bond [44]. However, Co(II) shows some preferential binding to N(imidazole) centers [Co–N(31), 2.046(1); Co–N(32), 2.076(9) Å] compared to its N(azo) cousin. The structures of transition metal complexes of RaaiR′ reveal that ruthenium(II) [29] and osmium(II) [31] prefer azo-N coordination while the imidazole-N center is preferred by palladium(II) [26,27] and platinum(II) [28]. Back donation ability of the metal center may distinguish the binding preferences. High spin cobalt(II) ($t_{2g}^5e_g^2$) is not a good π-donor [44] to form a strong Co–N(azo) bond and hence elongation of this bond length is recommended. Two axial Co–N distances [Co–N(31) and Co–N(4)] are shorter than their respective twins [Co–N(32) and Co–N(11)]. This supports axial compression. The azido N–N–N bond lengths and angles are as usual [35]. The N=N(azo) bond lengths [N(11)–N(21), 1.275(6); N(12)–N(22), 1.266(4) Å] are longer than the free ligand value (1.250(1) Å) [45,46]. This small elongation (~ 0.02 Å) may be due to steric requirement of the chelated azoimine group as well as weak d(Co) → π*(azo) back bonding charge transference.

3.2.2. [Co(MeaaiMe){(μ-1)N_3}{μ-(1,1)N_3}]$_2$ (**5b**)

The single crystal structure of the dimer **5b** is shown in Fig. 2. Selected bond distances and angles are given in Table 3. The CoN_5 coordination sphere around each Co(II) is distorted square pyramidal as can be seen from the angles subtended at the metal ion (Table 3). MeaaiMe binds in a usual chelating fashion and the chelate angle is 74.33(9)°. The molecule shows a center of inversion and the bridging parallelogram is constructed by Co_2N_2 (N(azido)) atom participation. The bridging angles are Co–N(8)–Co*, 98.55(10)° and N(8)–Co–N(8)*, 81.45(9)°. The azido (N_3) group bridges the two cobalt centers in a μ-(1,1) fashion. The five Co–N bond lengths in **5b** are comparatively less than the respective Co–N bond lengths from the mononuclear compound Co(MeaaiMe)$_2$(N_3)$_2$ (**3b**). It may be due to a steric effect provided by two chelate rings in **3b**. The Co–N(azo) [Co–N(1), 2.328(2) Å] bond length is longer than Co–N(imidazole) distances [Co–N(2), 2.010(2) Å]. The axial Co–N(azido) [Co–N(5), 1.948(2)] length is the shortest bond length in the Co–N series. The bridged Co–N(azido) distances are unequal [Co–N(8)*, 1.994(2); Co–N(8)*, 2.161(2) Å] showing a parallelogram pattern. Distortion in the square plane constituted by Co, N1, N2, N8, N(8)* is observed and the dihedral angle between the chelate plane (Co, N1, N3, C8, N2) and the bridged parallelogram (Co, N8, N(8)*, Co)* is 63°. Axial Co–N_3 (N5–N6–N7) is no longer perpendicular to the square plane and is leaning towards the imaginary edge of N(1)···N(8)* of the square plane. The bond angle data support this proposition: N1–Co–N5, 97.37(10)°; N2–Co–N5, 123.96(11)°; N8*–Co–N5, 94.17(11)°; N8*–Co–N5, 119.53(11)°. The bridged N_3 and axial –N_3 bond lengths and angles are as usual [36–41].

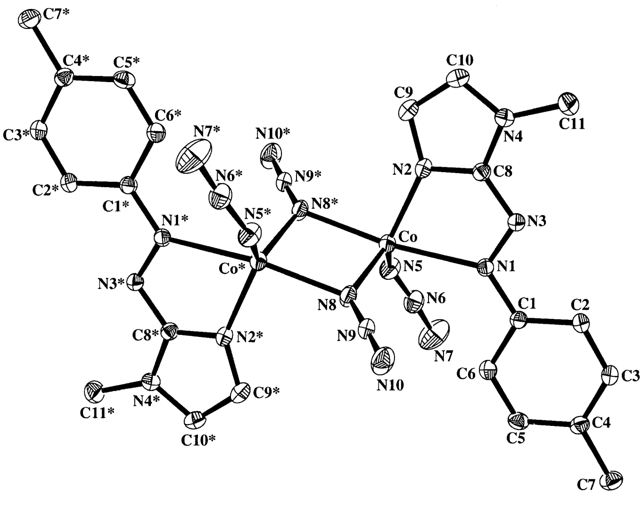


Fig. 2. ORTEP plot of [Co(MeaaiMe){μ-(1)N_3}{μ-(1,1)N_3}]$_2$ (**5b**).

Table 3
Selected bond distance (Å) and angles (°) for [Co(MeaaiMe)(N_3)$_2$(1,1-μ)]$_2$ (**5b**)

Bond distance (Å)		Bond angle (°)	
Co–N1	2.328(2)	N1–Co–N2	74.33(9)
Co–N2	2.010(2)	N1–N3–C8	112.0(2)
Co–N5	1.948(2)	N1–Co–N8	96.84(9)
Co–N8	1.994(2)	N1–Co–N8*	167.54(9)
Co–N8*	2.161(2)	N2–Co–N8*	95.28(9)
N1–N3	1.278(3)	N2–Co–N8	116.49(10)
N5–N6	1.167(4)	N2–Co–N5	123.96(11)
N6–N7	1.148(5)	N1–Co–N5	97.37(10)
N8–N9	1.204(4)	N3–C8–N2	126.0(3)
N9–N10	1.137(4)	Co–N2–C8	114.67(19)
N3–C8	1.368(4)	Co–N1–N3	112.89(17)
N2–C8	1.331(4)	N8–Co–N8*	81.45(9)
Co···Co*	3.151	Co–N8–Co*	98.55(10)
		N5–Co–N8	119.53(11)
		N5–Co–N8*	94.17(11)
		Co–N5–N6	135.9(3)
		N5–N6–N7	176.0(4)
		Co–N8–N9	133.8(2)
		Co*–N8–N9	125.11(19)
		N8–N9–N10	178.1(3)

3.3. Spectral studies

The IR spectra of the complexes were recorded on KBr discs in the range 4000–200 cm^{-1}. The bands were assigned on comparing with free ligand data. The most significant observation is the appearance of a very strong sharp single band at 2030–2045 cm^{-1} for **3/4** and a doublet at 2090–2095 and 2050–2060 cm^{-1} for **5/6**. These correspond to $\nu_{asym}(N_3)$. This supports mononuclear mono-dentate N_3^- bonding in **3/4** [35] and bidentate bridging end-on (μ-(1,1)) type in **5/6** [36]. The chelated ligand RaaiR′ shows characteristic transmission at 1600–370 cm^{-1}. Moderately intense stretching at 1585–1600 and 1420–1430 cm^{-1} are due to ν(C=N) and ν(N=N), respectively [26–28].

Solution electronic spectra of the complexes were recorded in acetonitrile solution in the UV–Vis region (250–900 nm). The data are listed in Table 4. In the visible region the complexes exhibit an intense band ≤ 400 nm. These transitions are presumably due to intraligand π–π*/ and n–π* transitions [26,27]. There are three transitions in the range 470–640 nm. The intensity pattern of the bands are different; the transition 470–485 nm is of high intensity ($\varepsilon \sim 10^4$) and is sharp while the other two transitions 520–575 and 620–640 nm are weak ($\varepsilon \sim 10^2$–10^3) and broad. Based on the low intensities, low energy nature of these bands they are considered to be possible d–d transitions. The high intense transition at 470–485 nm may be assigned to MLCT transitions. The splitting pattern of d–d transitions support six coordinate distorted octahedral symmetry around the cobalt center [44]. The coordinating solvent MeCN may result in the required symmetry around cobalt(II) in bridged dinuclear molecules.

3.4. Magnetism

Bulk magnetic moment (μ) measurements of the complexes at room temperature (300 K) suggest high spin mononuclear and binuclear complexes (Table 4). [Co(RaaiR′)$_2$(N$_3$)$_2$] exhibit μ in the range 4.4–4.7 BM, slightly less than the spin only value. Binuclear complexes, [Co(RaaiR′){(μ-1)N$_3$}{μ(1,1)N$_3$}]$_2$ (**5/6**) show magnetic moment 3.6–3.8 BM. Reduced μ in binuclear derivatives (**5/6**) may be due to anti-ferromagnetic spin-coupling via μ-(1,1)-N$_3$ bridging. This is in support of end-on bridged azido complexes [36]. We have not been able to carry out variable temperature susceptibility measurements due to the lack of instrumental facilities.

3.5. Redox properties

The complexes exhibit both metal and ligand centred electroactivity in the potential range ±1.7 V versus Ag/AgCl, Cl$^-$ electrode. A representative voltammogram is shown in Fig. 3 and data are given in Table 5. The complexes display one quasireversible oxidation process as evident from the peak-to-peak separation, $\Delta E_p \geq 100$ mV. Mononuclear [Co(RaaiR′)$_2$(N$_3$)] (**3/4**) complexes show higher positive redox potential, 1.0–1.2 V than that of dinuclear derivatives, [Co(RaaiR′){(μ-1)N$_3$}{μ(1,1)N$_3$}]$_2$ (**5/6**), 0.8–1.0 V. The cathodic and anodic peak heights (I_{pc} and I_{pa}) are equal. The one-electron nature of the couple is confirmed on comparing

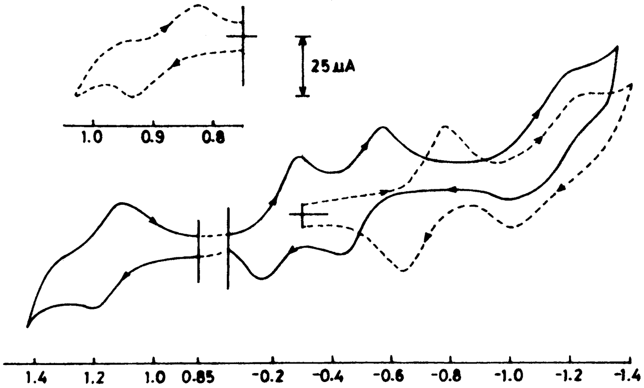


Fig. 3. Cyclic voltammogram of [Co(HaaiMe)$_2$(N$_3$)$_2$] (**3a**) (—) and [Co(HaaiMe){(μ-1)N$_3$}{(μ-1,1)N$_3$}]$_2$ (**5a**) (----) in acetonitrile using a Pt-disk electrode.

Table 4
UV–Vis spectra [a], IR [b] and magnetic moment (μ) data

Compound	UV–Vis spectral data (λ_{max} (nm)) (10^{-3} ε M^{-1} cm^{-1})	IR data			μ (BM)
		$\nu(N_3^-)$	ν(C=N)	ν(N=N)	
[Co(HaaiMe)$_2$(N$_3$)$_2$] (**3a**)	626(0.56), 575(0.61), 482(0.97), 406(13.08)	2035	1587	1426	4.34
[Co(HaaiEt)$_2$(N$_3$)$_2$] (**4a**)	624(0.42), 576(0.52), 485(1.223), 400(12.73)	2030	1596	1428	4.53
[Co(MeaaiMe)$_2$(N$_3$)$_2$] (**3b**)	626(0.34), 570(0.47), 484(1.01), 400(11.51)	2044	1598	1425	4.74
[Co(MeaaiEt)$_2$(N$_3$)$_2$] (**4b**)	624(0.26), 572(0.31), 480(1.55), 402(9.75)	2038	1595	1428	4.62
[Co(N$_3$){μ-(1,1)N$_3$}(HaaiMe)$_2$] (**5a**)	628(0.08), 570(0.79), 485(1.22), 404(7.83)	2090, 2056	1595	1420	3.71
[Co(N$_3$){μ-(1,1)N$_3$}(HaaiEt)$_2$] (**6a**)	624(0.54), 574(0.62), 484(1.56), 400(12.91)	2080, 2050	1591	1430	3.77
[Co(N$_3$){μ-(1,1)N$_3$}(MeaaiMe)$_2$] (**5b**)	630(0.63), 566(0.84), 480(2.12), 400(14.51), 380(2.36)	2085, 2053	1596	1427	3.76
[Co(N$_3$){μ-(1,1)N$_3$}(HaaiMe)$_2$] (**6b**)	628(0.51), 560(0.53), 474(2.39), 408(12.13)	2084, 2052	1595	1430	3.72

[a] Solvent: MeCN.

[b] In KBr disk.

Table 5
Voltammetric data

Compound	CV data E^0 (V) (ΔE_p, mV)	
	Co(II)/Co(III)	Ligand reduction
[Co(HaaiMe)$_2$(N$_3$)$_2$]	1.17(110)	−0.22(110), −0.50(140), −1.10(200)
[Co(MeaaiMe)$_2$(N$_3$)$_2$]	1.12(100)	−0.25(130), −0.53(140), −1.13(220)
[Co(HaaiEt)$_2$(N$_3$)$_2$]	1.13(120)	−0.24(110), −0.50(130), −1.15(190)
[Co(MeaaiEt)$_2$(N$_3$)$_2$]	1.06(100)	−0.32(120), −0.61(140), −1.37(240)
[Co(HaaiMe)(N$_3$)$_2$]$_2$	0.89(100)	−0.71(140), −1.13(200)
[Co(MeaaiMe)(N$_3$)$_2$]$_2$	0.80(110)	−0.65(120), −1.19(220)
[Co(HaaiEt)(N$_3$)$_2$]$_2$	0.81(100)	−0.64(110), −1.10(200)
[Co(MeaaiEt)(N$_3$)$_2$]$_2$	0.75(120)	−0.74(120), −1.20(220)

Solvent: MeCN, Pt-disk working electrode, Ag/AgCl, Cl$^-$ reference electrode, Pt-wire auxiliary electrode, supporting electrolyte, [^{n}Bu$_4$N][ClO$_4$] (0.01 M); solute concentration, 10^{-3} M; scan rate, 0.05 V s^{-1}; $\Delta E_p = |E_{pa} - E_{pc}|$, mV; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential, V; $E_{1/2} = 0.5(E_{pa} + E_{pc})$, V.

with the current height of the Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system. The complexes possess Co(II) and N$_3^-$ as oxidisable centers. On comparing with the electrochemical results of the cobalt(II)-2-(arylazo)pyridine system [47], the oxidative couple is assigned to Co(III)/Co(II). Presence of two π-acidic chelating RaaiR′ in mononuclear complexes **3/4** increases the Co(III)/Co(II) potential compared to one RaaiR′ ligand in dinuclear complexes (**5/6**). The more positive the potential, the stronger is the binding to the lower oxidation state. Thus, the mononuclear complexes show better stabilization to Co(II) than that of dinuclear species. The redox responses negative to reference electrode are referred to ligand reductions. The azo (−N=N−) group in the ligand RaaiR′ is known as a potential electron transfer center. Each ligand can accept two electrons in the electrochemically accessible LUMO which is predominantly azo in character [29,33]. So mononuclear complexes (**3/4**) may exhibit four one-electron ligand based reductions and dinuclear complexes **5/6** may show two reductions. We observed two one-electron quasireversible reductions ($\Delta E_p \geq 100$ mV) in the potential range −0.2 to −0.3 and −0.4 to −0.6 V in [Co(N$_3$)(RaaiR′)$_2$] (**3/4**) along with a two electron reduction (as evident from current height) at −1.0 to −1.3 V. Dinuclear complexes, **5/6** exhibit two quasireversible reductions at −0.6 to −0.7 V and −1.0 to −1.2 V.

3.6. EHMO calculation

X-ray crystallographic parameters of the complexes **3b** and **5b** have been used in the EHMO calculations of MOs. The energy of the HOMO and LUMO and their composition are set out in Table 6.

In general, the energy of the MOs of mononuclear complexes are higher than those of dinuclear bridged species. The HOMOs and LUMOs are composed of a function from cobalt, MeaaiMe and azido group. In Co(N$_3$)$_2$(MeaaiMe)$_2$ the ligand functions dominate to construct both the HOMO and LUMO: MeaaiMe contributes 60% in the HOMO and 81% in the LUMO (Table 6). Thus the high intense electronic spectral band which is HOMO → LUMO is considered as an intra-ligand-charge transfer transition. Additionally, the high energy weak band in the spectra are due to d–d transitions since both HOMO and LUMO contain 28 and 9% Co-atomic functions, respectively. Similar results are observed in the dinuclear bridged complex. The composition of the MOs suggests that the HOMO → LUMO charge transfer transition is associated with ILCT, MLCT and ligand-to-azido charge transferences. The HOMO, HOMO-1 and other lower energy orbitals are dominated by the metal atomic function. The oxidation process in the electrochemical experiment is referred to as electron extraction from the HOMOs. This proposition may suggest ligand oxidation. However, the observed results and the literature reports [47] account on Co(III)/Co(II) redox response at positive to the reference electrode system. Since the HOMO includes both metal and ligand functions in the ratio of about 1:2 we may assume that once the electron leaves from the ligand based functional portion, the metal electrons are piping out into it and ultimately we may observe metal centred oxidation. Besides, Co(III) is d^6, diamagnetic (t_{2g}^6) and hence the thermodynamic stability prefers to consider cobalt(II) oxidation. Thus the oxidation is referred to Co(II) → Co(III). The LUMOs are dominated by ligand orbitals and reduction is the accommodation of electrons in the LUMOs. Reductive responses are thus considered in general ligand reduction and in particular azo reductions.

4. Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic data center, CCDC No. 203078 for [Co(MeaaiMe)$_2$(N$_3$)$_2$] (**3b**) and CCDC No. 203079 for [Co(MeaaiMe){μ-(1)N$_3$}{μ-(1,1)N$_3$}]$_2$ (**5b**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 6

Compound	HOMO				LUMO			
	E_{HOMO} (eV)	% Co	% azide	% azo	E_{LUMO} (eV)	% Co	% azide	% azo
$[Co(MeaaiMe)_2(N_3)_2]$	−10.876	28	5	60(48)	−10.783	9		81(51)
$[Co(MeaaiMe)_2(N_3)\{\mu\text{-}(1,1)N_3\}]$	−11.889	16	4	59(10)	−11.796	53	25	10

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