

Naphthylazoimidazole complexes of cobalt(II): Synthesis structure and electrochemistry

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Abstract

The reaction of 1-alkyl-2-(naphthyl-(α/β)-azo)imidazoles [α -NaiR, (**1**) and β -NaiR (**2**) where R = Me (**a**), Et (**b**), CH₂Ph (**c**)] with Co(OAc)₂ · 4H₂O and NaN₃ in methanol solution has synthesised [Co(α/β -NaiR)₂(N₃)₂] (**3**, **4**). The complexes have been characterized by spectroscopic data and structurally confirmed by single crystal X-ray diffraction data in the case of [Co(β -NaiEt)₂(N₃)₂] (**4b**). The structure is a severely distorted tetrahedron of CoN₄ coordination in which β -NaiEt serves as a monodentate imidazole-N donor ligand. The distortion arises from two weak interactions from Co···N(azo) (N(azo) from β -NaiEt). Two weak transitions observed at >600 nm are due to the structural distortion. Cyclic voltammetry shows a high potential Co(III)/Co(II) couple along with ligand reductions in the complexes. The tris-chelates, [Co(NaiR)₃]²⁺, are also characterized.

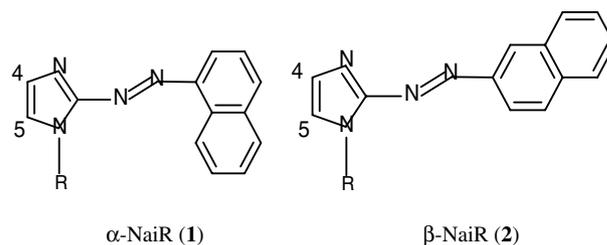
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Keywords: Naphthylazoimidazole; Co(II) complexes; Azide; Electrochemistry; X-ray structure

1. Introduction

Imidazole is ubiquitous in biology and chemistry [1]. This has encouraged the design of molecules with imidazole as one of the ligand platforms. In an effort towards the design of an imidazole containing azo system, we have synthesized arylazoimidazoles [2]. These ligands bear a π -acidic azoimine (—N=N—C=N—) function and have been utilized for the isolation of transition metal complexes of lower oxidation states [2–15]. The π -acidity of the chelating function is largely dependent on the nature of the heterocycle, the ring size, number of heteroatoms and substituents in the aryl group [16]. Use of naphthylamine during diazo coupling with imidazole has synthesized naphthylazoimidazole which has a higher steric crowding and better elec-

tron donating property [17] than the previously used 2-(phenylazo)imidazoles [12].



R = Me (**a**), Et (**b**), Bz (**c**)

In a continuation of our comprehensive studies on the coordinating properties of azoimidazoles, the present work is concerned with the synthesis and characterization of cobalt(II)-azide complexes of 1-alkyl-2-(naphthyl-(α/β)-azo)imidazoles (α -NaiR (**1**); β -NaiR (**2**)). Structural

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confirmation has been carried out by single crystal X-ray diffraction studies in one case.

2. Experimental

2.1. Materials

$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and NaN_3 were purchased from Loba Chemi, Bombay and 1-alkyl-2-(naphthyl-(α / β)-azo)imidazoles (α / β -NaiR) were prepared following the literature procedures [9]. All other chemicals and solvents were of reagent grade. Solvents were 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, reflectance spectra, JASCO UV–Vis/NIR model V-570; IR spectra (KBr disk, $4000\text{--}200\text{ cm}^{-1}$), JASCO FT-IR model 420. The room temperature magnetic moment was measured using a Vibrating sample 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. Electrochemical measurements were carried out with the use of computer controlled EG&G PARC VersaStat model 250 electrochemical instruments using a Pt-disk working electrode. The solution was IR compensated and the results were collected at 298 K. The reported results are referenced to SCE in acetonitrile and are uncorrected for junction potentials. Estimation of cobalt was carried out by the complexometric titration method [18].

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

2.3. Preparation of bis-chelated azido complexes,

$[\text{Co}(\alpha\text{-NaiEt})_2(\text{N}_3)_2]$ (**3b**)

1-Ethyl-2-(naphthyl- α -azo)imidazole (α -NaiEt) (0.06 g, 0.50 mmol) in MeOH (10 ml) was added dropwise to a stirred solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.062 g, 0.25 mmol) in MeOH (10 ml) at 298 K. The brown solution was stirred for 15 min. Then NaN_3 (0.03 g, 0.50 mmol) in MeOH (10 ml) was added to the brown solution. The color changed from brown to deep brown. The solution was filtered and then left undisturbed for a week. Dark brown crystals were obtained, which were washed with water, methanol and ether. Finally, they were dried *in vacuo*. The yield was 0.12 g, (75%). The microanalytical data of the complexes are as follows: $[\text{Co}(\alpha\text{-NaiMe})_2(\text{N}_3)_2]$ (**3a**): *Anal.* Calc. for $\text{C}_{28}\text{H}_{24}\text{N}_4\text{Co}$: C, 54.64; H, 3.90; N, 31.87; Co, 9.58. Found: C, 54.71; H, 4.01; N, 31.78; Co, 9.50%. $[\text{Co}(\alpha\text{-NaiEt})_2(\text{N}_3)_2]$ (**3b**): *Anal.* Calc. for $\text{C}_{30}\text{H}_{28}\text{N}_4\text{Co}$: C,

55.99; H, 4.35; N, 30.48; Co, 9.16. Found: C, 55.71; H, 4.45; N, 30.28; Co, 9.12%. $[\text{Co}(\alpha\text{-NaiBz})_2(\text{N}_3)_2]$ (**3c**): *Anal.* Calc. for $\text{C}_{36}\text{H}_{32}\text{N}_4\text{Co}$: C, 60.08; H, 4.45; N, 27.26; Co, 8.19. Found: C, 60.01; H, 4.40; N, 27.19; Co, 8.12%.

2.4. Preparation of $[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (**4b**)

1-Ethyl-2-(naphthyl- β -azo)imidazole (β -NaiEt) (0.06 g, 0.50 mmol) in MeOH (10 ml) was added dropwise to a stirred solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.062 g, 0.25 mmol) in MeOH (10 ml) at 298 K. The brown solution was stirred for 15 min. Then NaN_3 (0.03 g, 0.50 mmol) in MeOH (10 ml) was added to the brown solution. The color changed from brown to deep brown. 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 0.11 g, (70%). The microanalytical data of the complexes are as follows: $[\text{Co}(\beta\text{-NaiMe})_2(\text{N}_3)_2]$ (**4a**): *Anal.* Calc. for $\text{C}_{28}\text{H}_{24}\text{N}_4\text{Co}$: C, 54.64; H, 3.90; N, 31.87; Co, 9.58. Found: C, 54.73; H, 4.06; N, 31.81; Co, 9.52%. $[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (**4b**): *Anal.* Calc. for $\text{C}_{30}\text{H}_{28}\text{N}_4\text{Co}$: C, 55.99; H, 4.35; N, 30.48; Co, 9.16. Found: C, 55.81; H, 4.41; N, 30.36; Co, 9.13%. $[\text{Co}(\beta\text{-NaiBz})_2(\text{N}_3)_2]$ (**4c**): *Anal.* Calc. for $\text{C}_{36}\text{H}_{32}\text{N}_4\text{Co}$: C, 60.08; H, 4.45; N, 27.26; Co, 8.19. Found: C, 60.03; H, 4.41; N, 27.21; Co, 8.13%.

2.5. Preparation of tris-chelates,

$[\text{Co}(\alpha\text{-NaiMe})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**5a**)

To a degassed dry ethanol solution (15 ml) of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.25 g, 0.68 mmol), α -NaiMe (0.58 g, 2.46 mmol) in the same solvent (15 ml) was added under N_2 and stirred continuously. The solution colour turned to deep brown-violet. It was then refluxed for 8 h. Excess of LiClO_4 (5 mmol) in MeOH (5 ml) was added. Nitrogen gas was bubbled through this solution to reduce its volume to half of its original value and the flask was corked and kept at 10°C for 18 h. Brown crystals deposited on the glass wall were collected by filtration, washed with ethanol and stored over CaCl_2 . Yield: 0.25 g (37%). The purity of the compound was checked by microanalytical data. The compounds are sensitive to moisture and were kept under dry conditions. Microanalytical data of the complex is as follows: $[\text{Co}(\alpha\text{-NaiMe})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**5a**) *Anal.* Calc. for $\text{C}_{42}\text{H}_{38}\text{N}_{12}\text{Cl}_2\text{O}_9\text{Co}$: C, 51.22; H, 3.66; N, 17.07. Found: C, 51.31; H, 3.71; N, 17.18%. All other complexes were prepared by the same procedure. The yield varied from 35% to 40% and microanalytical data of the complexes are as follows. $[\text{Co}(\alpha\text{-NaiEt})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**5b**) *Anal.* Calc. for $\text{C}_{45}\text{H}_{44}\text{N}_{12}\text{Cl}_2\text{O}_9\text{Co}$: C, 52.64; H, 4.09; N, 16.38. Found: C, 52.59; H, 4.17; N, 16.29%. $[\text{Co}(\beta\text{-NaiMe})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**6a**) *Anal.* Calc. for $\text{C}_{42}\text{H}_{38}\text{N}_{12}\text{Cl}_2\text{O}_9\text{Co}$: C, 51.22; H, 3.66; N, 17.07. Found: C, 51.30; H, 3.74; N, 17.16. $[\text{Co}(\alpha\text{-NaiEt})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**6b**) *Anal.* Calc. for $\text{C}_{45}\text{H}_{44}\text{N}_{12}\text{Cl}_2\text{O}_9\text{Co}$: C, 52.64; H, 4.09; N, 16.38. Found: C, 52.58; H, 4.15; N, 16.27%.

2.6. X-ray crystal structure analysis of $[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (**4b**)

The crystals were grown by slow evaporation of the reaction mixture over a week. Data were collected with a Bruker CCD area detector diffractometer [19] using fine-focus sealed graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 295(2) K for **4b**. Diffractions were recorded with 2θ in the range $3.84 \leq 2\theta \leq 56.62^\circ$. A summary of the crystallographic data and structure refinement parameters are given in Table 1. Reflection data were recorded using the ψ and ω scan techniques. Data were corrected for Lp and an empirical absorption correction [20] in the hkl range: $-25 \leq h \leq 25$; $-17 \leq k \leq 18$; $-17 \leq l \leq 17$. Data reduction was carried out using the SAINT program [20]. In order to restrain the anisotropic displacements, we used several DELU and SIMU instructions in the refinement, so the number of restrained parameters is a little larger. The structure was solved by the direct method using SHELXS-97 [21] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using the riding model. The molecular graphics were carried out using ORTEP-3 for Windows [21]. In the final difference Fourier map, the residual maxima and minima Δ_{max} (e \AA^{-3}), 0.342 and Δ_{min} (e \AA^{-3}), -0.264 for **4b** were carried out using SHELXL-97 [22], indicating that there is no solvent in the crystal.

Table 1
Summarised crystallographic data for $[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (**4b**)

	$[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (4b)
Empirical formula	$\text{C}_{30}\text{H}_{28}\text{N}_{14}\text{Co}$
Formula weight	643.59
Temperature (K)	295(2)
Crystal system	monoclinic
Space group	$C2/c$
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.20$
Unit cell dimensions	
a (\AA)	19.2314(13)
b (\AA)	14.0994(9)
c (\AA)	13.4699(9)
β ($^\circ$)	123.3860(10)
V (\AA^3)	3049.7(3)
Z	4
λ (\AA)	0.71073
μ (Mo $K\alpha$) (mm^{-1})	0.609
D_{calc} (g cm^{-3})	1.402
Refined parameters	204
Total reflection	3706
Unique data [$I > 2\sigma(I)$]	2647
R_1^a [$I > 2\sigma(I)$]	0.0554
wR_2^b	0.1198
Goodness-of-fit	0.938

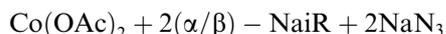
^a $R_1 = \sum |F_o - F_c| / \sum F_o$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0800P)^2]$ for **4b** where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

3.1. The complexes and their formulation

1-Alkyl-2-(naphthyl-(α/β)-azo)imidazoles, (α/β -NaiR), are used in this work. The reaction of 1-alkyl-2-(naphthyl-(α/β)-azo)imidazoles (α/β -NaiR), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and NaN_3 in any mole ratio [1:1:2, 1:2:2; 1:1:excess (>4 mole)] in MeOH affords complexes of the formulae $[\text{Co}(\alpha/\beta\text{-NaiR})_2(\text{N}_3)_2]$ (**3**, **4**).



The complexes are non-electrolytes in MeCN. The composition of the complexes was supported by microanalytical data. Room temperature (298 K) magnetic moment measurements show high spin data in the range 4.9–5.2 B.M.

3.2. Structure description of $[\text{Co}(\text{N}_3)_2(\beta\text{-NaiEt})_2]$ (**4b**)

The molecular structure of $[\text{Co}(\text{N}_3)_2(\beta\text{-NaiEt})_2]$ (**4b**) is shown in Fig. 1. The bond distances and angles are set out in Table 2. The structure is a severely distorted tetrahedron with C_{2v} symmetry. The cobalt(II) centre is surrounded by two N(imidazole) donor atoms from two β -NaiEt ligands and two azide-N atoms. β -NaiEt has two N-centres: N(imidazole) and N(azo). It could serve as a monodentate imidazole-N donor or N(azo), N(imidazole)

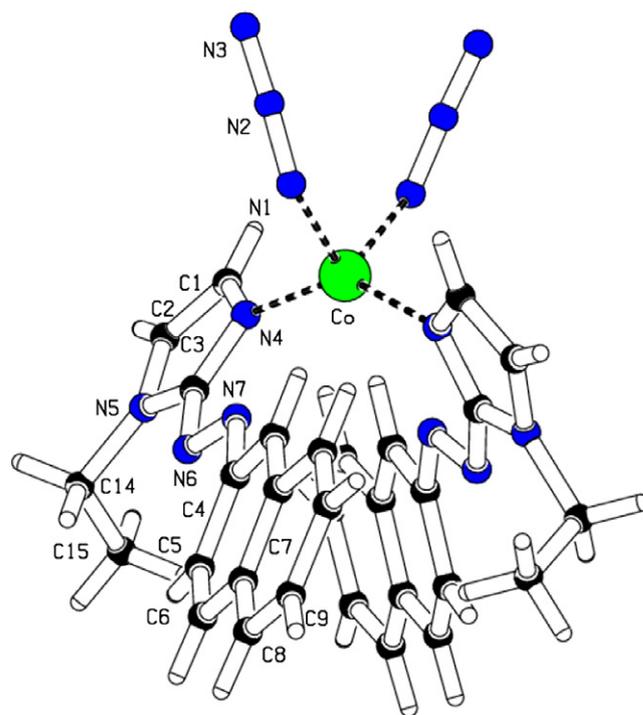


Fig. 1. ORTEP view of $[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (**4b**) with 30% probability ellipsoids.

Table 2
Selected bond distance (Å) and angles (°) for [Co(β -NaiEt)₂(N₃)₂] (**4b**)

Bond distance (Å)		Bond angle (°)	
Co—N(4)	2.0428(16)	N(1)—Co—N(1*) ^a	102.79(14)
Co—N(1)	1.992(2)	N(1)—Co—N(4)	110.29(8)
N(1)—N(2)	1.195(3)	N(1)—Co—N(4*) ^a	92.99(8)
N(2)—N(3)	1.148(3)	N(4)—Co—N(4*) ^a	142.73(10)
N(6)—N(7)	1.252(2)	N(6)—N(7)—C(4)	113.84(17)
N(4)—C(3)	1.303(3)	N(7)—N(6)—C(3)	110.07(17)
N(5)—C(2)	1.357(3)	N(2)—N(1)—Co	134.66(16)
N(5)—C(3)	1.366(2)	N(1)—N(2)—N(3)	175.4(2)
N(6)—C(3)	1.407(3)	C(3)—N(4)—Co	123.62(13)
N(7)—C(4)	1.420(2)	C(1)—N(4)—Co	130.90(16)

^a Symmetry: 1 - x, 1 + y, 1.5 - z.

bidentate chelating agent. Forced chelation with the azoimine ($-\text{N}=\text{N}-\text{C}=\text{N}-$) function gives a very long Co—N(azo) distance (2.6844(1) Å) and low chelate angle (N(azo)—Co—N(imidazole), 66.22(5)°). The Co—N(imidazole) (2.0428(16) Å) distances are of reasonable length and are comparable with reported data [13,23]. The distortion may arise from the long Co...N(azo) distance. So, the structure may be considered as a tetrahedron with two additional weak interactions. In 1-alkyl-2-(arylaazo)imidazole (RaaiR') complexes of Co(II) we have isolated octahedral complexes when azide N₃⁻ is present as the counter ion [13]. In the presence of ClO₄⁻ as a counter ion we have isolated tetrahedral [Co(RaaiR')₄]²⁺ where the ligands bind through N(imidazole) only, [19] which upon reaction with

N₃⁻ or NCS⁻ have isolated octahedral complexes Co(RaaiR')₂(X)₂ (X = N₃⁻ or NCS⁻). That means azoimidazole may bind Co(II) as a monodentate imidazole-N or bidentate N(imidazole), N(azo) ligand [13,23]. There is a small difference in CFSE between octahedral and tetrahedral symmetry of high-spin Co(II) complexes and hence the steric reason is the determining factor in the geometrical preference of the complex. The naphthyl group is sterically more crowded than the pendant aryl group in azoimidazoles, which may lead to the generation of the distorted tetrahedral Co(II) geometry in the present case. The Co—N(azido) bond length is comparable with the reported data [13]. The N=N bond length is 1.252(2) Å in **4b**. Although data are not available for this ligand system, its isomeric analogue 1-ethyl-2-(naphthyl- α -azo)imidazolium hexafluorophosphate shows 1.267(3) Å for the N=N length [11]. The N—N—N bond parameters lie within the reported range [13,24]. An intermolecular hydrogen bonded unit is constituted by interaction between the imidazole C(2)—H(2) of one molecule with the azide—N(3) of a neighbouring molecule: (C(2)—H(2)...N(3): C(2)—H(2), 0.93 Å, H(2)—N(7), 2.54 Å, C(2)...N(3), 3.370(1) Å and \angle C(2)—H(2)...N(3), 149.22°). The existence of C—H... π (Cg) (Fig. 2) (C(13)—H(13)...Cg(1), 2.796(8) Å; C(15)—H(15B)...Cg(2), 3.390(5) Å) and π ... π interactions (face-to-face type) (Cg(1)—Cg(2), 4.305(4) Å; Cg(1)—Cg(3), 4.039(7) Å; Cg(2)—Cg(2), 4.389(6) Å) increases the robustness of the structure (Cg(1): N(4)—C(1)—N(5)—C(2)—C(3);

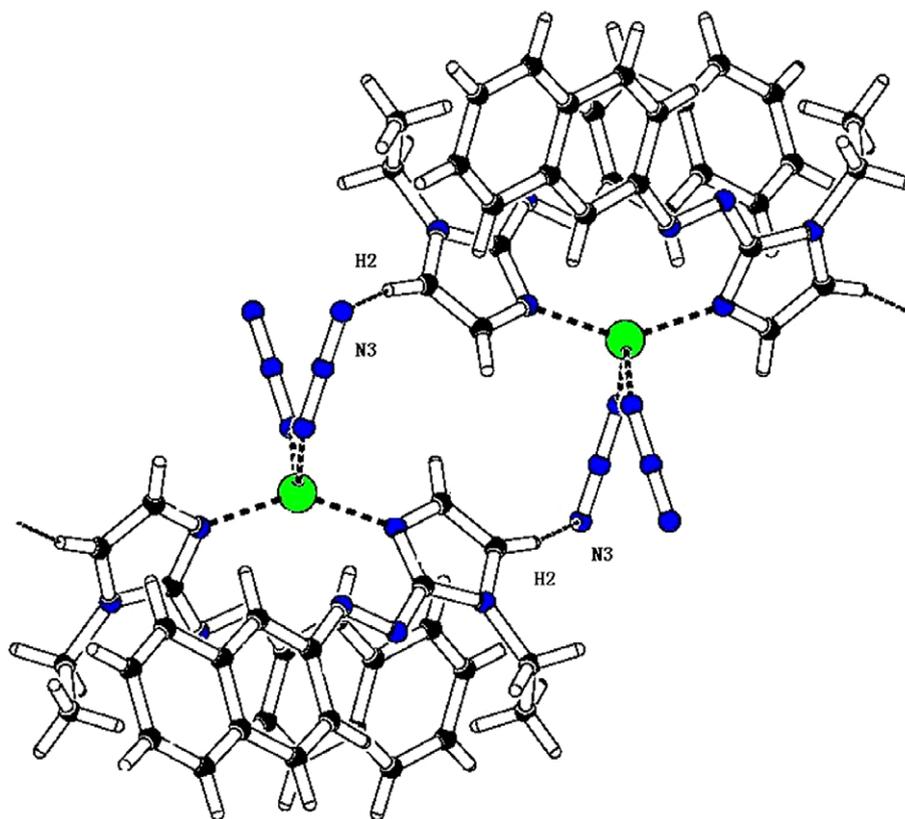


Fig. 2. Packing of two molecules.

Cg(2): C(4)–C(5)–C(6)–C(7)–C(12)–C(13); Cg(3): C(7)–C(8)–C(9)–C(10)–C(11)–C(12); symmetry, $1/2 - x, 1/2 - y, 1 - z$.

3.3. Spectral studies

The IR bands were assigned by comparing with the free ligand data. The most significant observation is the appearance of a very strong sharp single band at 2035–2045 cm^{-1} . This corresponds to $\nu_{\text{asym}}(\text{N}_3^-)$. This supports the mononuclear monodentate N_3^- bonding in the complexes. The ligand α/β -NaiR shows characteristic vibrations at 1600–370 cm^{-1} . Moderately intense stretchings at 1570–1600 and 1435–1440 cm^{-1} are due to $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$, respectively.

The 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 3. In the visible region both types of complexes exhibit an intense band ≤ 400 nm. These transitions are presumably due to intra-ligand $\pi-\pi^*$ and $n-\pi^*$ transitions. The structural distortion undoubtedly effects the spectral transitions and intensity of the bands [25]. High-spin tetrahedral Co(II) complexes may exhibit two or three weak transitions at the visible

to near-IR region. However, the intensity of these bands is very much dependent on the degree of distortion of the structures [26]. In the present example, the structural distortion from regular tetrahedron arises from weak $\text{Co}\cdots\text{N}(\text{azo})$ (*vide supra*) interactions. There are three transitions in the range 415–640 nm for complexes **3**. The intensity patterns of the bands are different; the transitions 415–425 and 440–455 nm are highly intense ($\epsilon \sim 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$) and sharp, while the transition 630–640 nm is weak ($\epsilon \sim 180\text{--}450 \text{ mol}^{-1} \text{ cm}^{-1}$) and very broad. Based on the low intensity and low energy, the band at 630–640 nm may be due to d–d transitions [26]. The high intense bands at 415–455 nm may be assigned to MLCT transitions. The complexes **4** also exhibit three transitions in the range 445–675 nm. The transition 440–445 nm is of high intensity ($\epsilon \sim 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$) and is sharp, while the other two transitions at 600–615 and 660–670 nm are weak and broad.

3.4. Cyclic voltammetry

Representative voltammograms are shown in Fig. 3 and data are collected in Table 4. The complexes display one oxidation couple at 1.3–1.5 V and $I_{\text{pa}}/I_{\text{pc}}$ equals 0.9–1.0.

Table 3

UV–Vis spectra^a, IR and magnetic moment (μ) data of $[\text{Co}(\alpha/\beta\text{-NaiR})_2(\text{N}_3)_2]$ (**3a**, **3b**) and $[\text{Co}(\alpha/\beta\text{-NaiR})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**5a**, **6b**)^b

Compound	UV–Vis spectral data ($\lambda_{\text{max}}/\text{nm}$) ($10^{-3} \epsilon \text{ M}^{-1} \text{ cm}^{-1}$)	IR data			
		$\nu_{\text{N}_3^-}$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	μ (B.M.)
$[\text{Co}(\alpha\text{-NaiMe})_2(\text{N}_3)_2]$ (3a)	632(0.24), 452(7.76), 422(8.71), 392(12.24)	2035	1598	1436	4.91
$[\text{Co}(\alpha\text{-NaiEt})_2(\text{N}_3)_2]$ (3b)	636(0.32), 444(7.44), 416(8.13), 396(14.21)	2034	1600	1438	5.06
$[\text{Co}(\alpha\text{-NaiBz})_2(\text{N}_3)_2]$ (3c)	634(0.27), 450(6.83), 417(7.91), 392(14.48)	2034	1598	1434	4.82
$[\text{Co}(\beta\text{-NaiMe})_2(\text{N}_3)_2]$ (4a)	668(0.18), 602(0.32), 451(9.80), 394(12.02)	2036	1598	1435	4.21
$[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (4b)	672(0.29), 612(0.41), 448(10.05), 396(14.05)	2038	1597	1438	4.18
$[\text{Co}(\beta\text{-NaiBz})_2(\text{N}_3)_2]$ (4c)	665(0.21), 604(0.38), 448(9.98), 396(13.60)	2038	1598	1436	4.24
$[\text{Co}(\alpha\text{-NaiMe})_3](\text{ClO}_4)_2$ (5a)			1595	1398	1.65
$[\text{Co}(\alpha\text{-NaiEt})_3](\text{ClO}_4)_2$ (5b)			1597	1395	1.58
$[\text{Co}(\beta\text{-NaiMe})_3](\text{ClO}_4)_2$ (6a)			1598	1398	1.73
$[\text{Co}(\beta\text{-NaiEt})_3](\text{ClO}_4)_2$ (6b)			1596	1396	1.67

^a Solvent: MeCN.

^b Mixture of isomers, $\nu(\text{ClO}_4)$ at 1120–1100, 1090–1080 cm^{-1} .

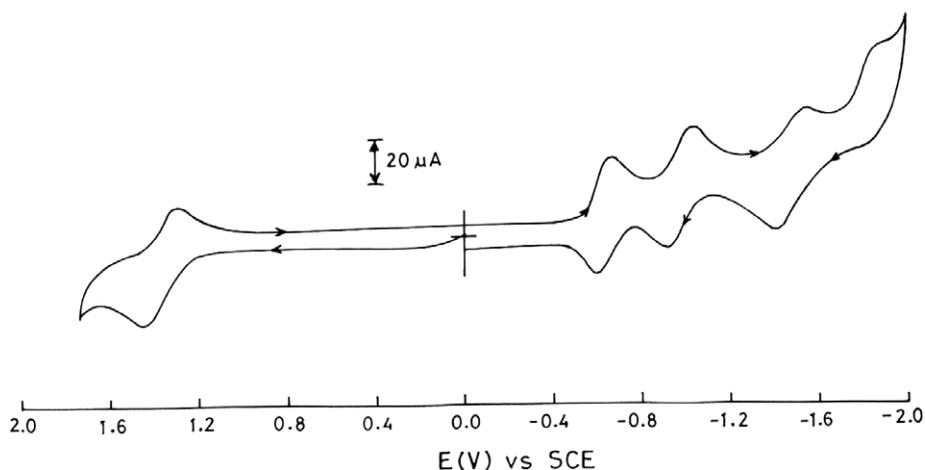


Fig. 3. Cyclic voltammogram of $\text{Co}(\alpha\text{-NaiMe})_2(\text{N}_3)_2$ (**3a**).

Table 4
Cyclic voltammetric data of $[\text{Co}(\alpha/\beta\text{-NaiR})_2(\text{N}_3)_2]$ (**3**, **4**)^a

Compound	Co(III)/Co(II)	Ligand reductions			
$[\text{Co}(\alpha\text{-NaiMe})_2(\text{N}_3)_2]$ (3a)	1.46 (120)	-0.58 (120)	-0.98 (130)	-1.30 (160)	-1.59 ^b
$[\text{Co}(\alpha\text{-NaiEt})_2(\text{N}_3)_2]$ (3b)	1.43 (130)	-0.62 (120)	-0.95 (120)	-1.43 (140)	-1.60 ^b
$[\text{Co}(\alpha\text{-NaiBz})_2(\text{N}_3)_2]$ (3c)	1.47 (120)	-0.60 (130)	-0.90 (150)	-1.38 (150)	-1.60 ^b
$[\text{Co}(\beta\text{-NaiMe})_2(\text{N}_3)_2]$ (4a)	1.37 (130)	-0.64 (140)	-0.98 (120)	-1.44 (160)	-1.62 ^b
$[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (4b)	1.33 (120)	-0.70 (130)	-1.02 (130)	-1.37 (160)	-1.60 ^b
$[\text{Co}(\beta\text{-NaiBz})_2(\text{N}_3)_2]$ (4c)	1.39 (120)	-0.64 (120)	-0.94 (140)	-1.30 (180)	-1.60 ^b

^a Solvent, MeCN; working electrode, Pt-disk milli electrode, Pt-wire auxiliary, SCE reference; supporting electrolyte $[\text{nBu}_4\text{N}][\text{ClO}_4]$; scan rate 0.05 V s^{-1} , potential $E_{1/2} = 0.5(E_{\text{pa}} + E_{\text{pc}})$, $\Delta E_{\text{p}} = |E_{\text{pa}} - E_{\text{pc}}|$, mV; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential.

^b E_{pc} .

Although the peak heights are not equivalent for the various complexes, the areas under the peaks are comparable. The peak-to-peak separation is $>120 \text{ mV}$. This supports the quasireversibility of the couple. The oxidation couple refers to the Co(III)/Co(II) response. Azo ($-\text{N}=\text{N}-$) is a good π -acidic function and can assist $d\pi \rightarrow \pi^*$ (azo) charge transfer, which effectively stabilizes the lower oxidation state. The data in Table 4 suggest that Co(II) could be better stabilized in $\text{Co}(\alpha\text{-NaiR})_2(\text{N}_3)_2$ than in $\text{Co}(\beta\text{-NaiR})_2(\text{N}_3)_2$. There are three observable quasireversible to irreversible reduction couples appearing at -0.6 to -0.7 V , -1.3 to -1.4 V and $<-1.6 \text{ V}$. Naphthylazoimidazole is an eligible reducing ligand. The azo ($\text{N}=\text{N}$) group is a potential electron receiving centre. Each ligand can accommodate two electrons corresponding to $[-\text{N}=\text{N}-]/[-\text{N}=\text{N}-]^-$ and $[-\text{N}=\text{N}-]^-/[-\text{N}-\text{N}-]^-$ redox responses. In principle there will be four redox couples. However, we observed three reductive responses. $\alpha\text{-NaiR}$ is thermodynamically more stable than $\beta\text{-NaiR}$ and this is supported by higher redox potential data of the respective cobalt complexes.

3.5. Tris- $\{1\text{-alkyl-2-(naphthyl-(\alpha/\beta)\text{-azo})imidazole}\}$ -cobalt(II) perchlorate monohydrate, $[\text{Co}(\alpha/\beta\text{-NaiR})_3]-(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

The brown complexes of $[\text{Co}(\text{NaiR})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**5**, **6**) have been prepared by stirring $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NaiR in the mole proportion 1:3.5 in dry ethanol under N_2 atmosphere and have been isolated as the monohydrate perchlorate salt by adding NaClO_4 under cold conditions. A very dry condition is absolutely necessary to get the pure product. On exposure to air the brown crystalline shining compound becomes moistened and results in an impure gummy compound. Because of its moisture sensitivity we could not crystallise this compound to get an X-ray quality crystal. In a dry inert atmosphere the compound is highly stable. In solution the complex is unstable and presumably dissociates to the solvato species $[\text{Co}(\text{NaiR})_2(\text{S})_2]^{2+}$. Upon addition of NaN_3 to an ethanolic solution of the complex, it immediately separates into $[\text{Co}(\text{NaiR})_2(\text{N}_3)_2]$, which has been proved by spectral (IR, UV-Vis), magnetic, conductance data and on comparing with the previously prepared complex (*vide supra*). All our attempts to prepare $\text{Co}(\text{NaiR})_2\text{Cl}_2$ using CoCl_2 and NaiR in different metal:ligand ratios, and even by addition of LiCl to an alcoholic solution of $\text{Co}(\text{ClO}_4)_2$ and NaiR, have failed.

$\text{Co}(\text{NaiR})_3(\text{ClO}_4)_2$ is sufficiently stable in dry inert atmosphere. Solid state bulk magnetic moment measurements establish this conjecture. Initial measurement of the moment immediately after removal from a dessicator gives a magnetic moment corresponding to a low-spin electron configuration ($t_{2g}^6 e_g^1$, μ , $\sim 1.8 \text{ B.M.}$). Exposure to air for a week in the same sample tube gives a moment much higher than the low-spin value, although it is lower than the spin-free ($t_{2g}^5 e_g^2$) value. This suggests the formation of a mixture of low-spin and high-spin complexes. The azido complexes, $\text{Co}(\text{NaiEt})_2(\text{N}_3)_2$ are a high-spin system. Air oxidation of cobalt(II)-azoimine complexes has been ruled out from the literature report [13,23,26].

The complexes show a very strong and structured vibration at $1120\text{--}1110$, $1100\text{--}1090 \text{ cm}^{-1}$, and a sharp, medium intense band at 630 cm^{-1} . This is assigned to the ClO_4^- vibration. The structured stretching may be due to reduction in Td symmetry of the ion by a hydrogen-bonding interaction with crystallized H_2O and/or $\text{C-H} \cdots \text{O}(\text{ClO}_3)$. A strong and sharp stretch at $1590\text{--}1600 \text{ cm}^{-1}$ is due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ while another stretch at $1400\text{--}1390 \text{ cm}^{-1}$ is referred to $\nu(\text{N}=\text{N})$. The stretching vibration of the water of crystallization appears as a broad medium band centred at 3450 cm^{-1} .

Tris-chelates with unsymmetric N, N' donor centre may, in principle, exist in two different isomeric forms: facial and meridional [27]. Additionally, tris-chelates undergo quick ligand dissociation to give bis-chelated solvato species. So we logically assume that the spectral transitions may be the combination of similar transitions from several isomers present in the solution. Similarly studies on the redox properties by solution electrochemistry of these complexes do not bring any definite conclusion. Thus, we are not interested in extending the solution studies of the tris-chelates.

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4. Conclusion

This paper describes the mononuclear bis-azido Co(II) complexes of 1-alkyl-2-(naphthyl-(α/β)-azo)imidazoles. The complexes are characterized by different physicochemical

methods and single crystal X-ray structure determination in one case shows a distorted tetrahedral CoN_4 coordination arrangement. The complexes show high potential Co(III)/Co(II) redox couples along with azo reductions.

5. Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic data center, CCDC No. 251235 for $[\text{Co}(\beta\text{-NaiEt})_2(\text{N}_3)_2]$ (**4b**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>).

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