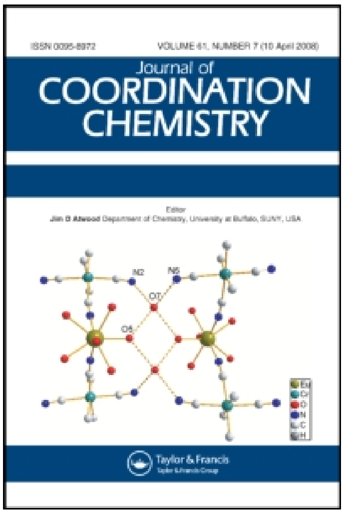

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Nickel(II)-azido/thiocyanato complexes of 1-alkyl-2-(arylazo) imidazole: single crystal X-ray structure of [Ni(Pai-Me)$_2$(N$_3$)$_2$] (Pai-Me = 1-methyl-2(phenylazo)imidazole)

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Reaction of Ni(ClO$_4$)$_2$·6H$_2$O with 1-alkyl-2-(arylazo)imidazole (RaaiR$^{/}$) and sodium azide (NaN$_3$) or ammonium thiocyanate (NH$_4$SCN) (1 : 2 : 2 molar ratio) in methanol gives [Ni(RaaiR$^{/}$)$_2$(X)$_2$] (X=N$_3$ (**3**, **4**) and SCN (**5**, **6**). All these complexes are characterized by elemental analyses, UV–Vis and IR spectral data, thermal and magnetic moment measurements. The X-ray structure is confirmed by single crystal measurement of [Ni(Pai-Me)$_2$(N$_3$)$_2$] (**3a**). Cyclic voltammetry exhibits quasireversible response at >0.80 V corresponding to Ni(III)/Ni(II) couple along with ligand reductions at negative potential (< -0.5 V) to SCE reference. The electronic structure, spectral and redox properties are explained by DFT (Gaussian03) calculation.

Keywords: Nickel(II)-azido/thiocyanato complexes; Arylazoimidazoles; X-ray structure; Electrochemistry; DFT calculation

1. Introduction

Heterocyclic compounds are widely distributed in nature and essential to life in various forms. Metal complexes of heterocycles have applications from catalysis, redox and photoactive materials, organic synthesis, drug discovery, etc. The design of ligands having π-deficient N-heterocycles for transition metals is an active area of current research [1, 2]. Imidazole, a five-membered N-heterocycle, has special importance because of its ubiquity in chemistry and biology. Molecules consisting of one imidazole ring with a pendant azo-N donor, known as arylazoimidazoles, are excellent π-acidic ligands [3, 4]. Transition metal coordination chemistry of the azoimine function (–N=N–C=N–) is rapidly expanding in areas ranging from organometallic chemistry, metal assisted organic transformation, radical chemistry, redox chemistry, stabilization of lower oxidation state metal ions, solid phase extraction, anticancer drugs, photophysical studies [4–13], etc. The present work stems from our effort to explore

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3d block chemistry of 1-alkyl-2-(arylazo)imidazole (RaaiR$^{/}$) [14]. Herein we describe nickel(II)-azido and -thiocyanato complexes of RaaiR$^{/}$. The electronic structure, spectral and redox properties are explained by DFT calculation (Gaussian 03) in a representative case.

2. Experimental

2.1. *Materials*

$Ni(ClO_4)_2 \cdot 6H_2O$ was prepared by adding $NiCO_3$ to warm aqueous solution of $HClO_4$ on a steam bath and subsequent slow evaporation in a $CaCl_2$ desiccator. NaN_3 and NH_4SCN were obtained from E. Merck, India and 1-alkyl-2-(arylazo)imidazoles (RaaiR$^{/}$) were prepared by reported procedure [4]. All other chemicals and solvents are reagent grade; solvents were dried [15].

2.2. *Physical measurements*

Microanalytical (C, H, N) data were obtained from a Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis, Perkin Elmer Lambda-25; FT-IR (KBr disk, 4000–400 cm^{-1}), Perkin Elmer RX-1 and JASCO Model 420 (4000–200 cm^{-1}) spectrophotometers. Electrical conductivity in MeCN solution was measured with a Systronics 304 digital conductivity meter with a solution concentration of ca 10^{-3} mol dm^3. Magnetic susceptibilities were obtained from a vibrating sample magnetometer PAR 155 model and data were corrected by subtracting diamagnetic contribution, calculated by Pascal's constants. Electrochemical measurements were carried out with a computer controlled EG & G PARC VersaStat model 250 Electrochemical instrument using a Pt-disk working electrode and Pt-wire auxiliary electrode under nitrogen. The solution was IR compensated and the results were collected at 298 K; results are referenced to SCE in MeCN and uncorrected for junction potential. $[n\text{-}Bu_4N][ClO_4]$ was used as supporting electrolyte.

2.3. *Synthesis of $[Ni(Pai\text{-}Me)_2(N_3)_2]$ (3a)*

Sodium azide (NaN_3) (0.90 g, 1.38 mmol) in MeOH (10 mL) was added to stirred solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.25 g, 0.68 mmol) in MeOH (10 mL) at 298 K. 1-Methyl-2-(phenylazo)imidazole (Pai-Me) (**1a**) (0.26 g, 1.40 mmol) in 20 mL MeOH was added dropwise to this solution. The resulting brown solution was stirred for 15 min, filtered and left undisturbed for a few days. The dark brown crystalline products were separated, collected, washed with aqueous methanol and finally with ether and dried *in vacuo*. Yield was 0.19 g (54%).

All other complexes were prepared by the same procedure. Crystalline products were obtained in yields of 50–70%.

Elemental analysis data were as follows: $[Ni(Pai\text{-}Me)_2(N_3)_2]$, **3a**: $C_{20}H_{20}N_{14}Ni$: Calcd: C, 46.63; H, 3.91; N, 38.06. Found: C, 46.58; H, 4.00; N, 38.00%. $[Ni(Tai\text{-}Me)_2(N_3)_2]$,

3b: $C_{22}H_{24}N_{14}Ni$: Calcd: C, 48.64; H, 4.45; N, 36.03. Found: C, 48.60; H, 4.51; N, 35.95. $[Ni(Pai\text{-}Et)_2(N_3)_2]$, **4a**: $C_{22}H_{24}N_{14}Ni$: Calcd: C, 48.64; H, 4.45; N, 36.03. Found: C, 48.68; H, 4.40; N, 36.15%. $[Ni(Tai\text{-}Et)_2(N_3)_2]$, **4b**: $C_{24}H_{28}N_{14}Ni$: Calcd: C, 50.46; H, 4.94; N, 34.33. Found: C, 50.40; H, 5.00; N, 34.28%. $[Ni(Pai\text{-}Me)_2(NCS)_2]$, **5a**: $C_{22}H_{20}N_{10}S_2Ni$: Calcd: C, 47.93; H, 4.93; N, 25.41. Found: C, 47.88; H, 4.85; N, 25.46%. $[Ni(Tai\text{-}Me)_2(NCS)_2]$, **5b**: $C_{24}H_{24}N_{10}S_2Ni$: Calcd: C, 50.10; H, 4.20; N, 24.35. Found: C, 50.00; H, 4.25; N, 24.41%. $[Ni(Pai\text{-}Et)_2(NCS)_2]$, **6a**: $C_{24}H_{24}N_{10}S_2Ni$: Calcd: C, 50.10; H, 4.20; N, 24.35. Found: C, 50.14; H, 4.24; N, 24.31%. $[Ni(Tai\text{-}Et)_2(NCS)_2]$, **6b**: $C_{26}H_{20}N_{10}S_2Ni$: Calcd: C, 51.74; H, 4.67; N, 23.21. Found: C, 51.70; H, 4.61; N, 23.26%.

2.4. *X-ray crystal structure analysis*

X-ray quality crystals of $[Ni(Pai\text{-}Me)_2(N_3)_2]$ (**3a**) were isolated from diffusion of 2-methoxy-ethanol solution of the complex to methanol at room temperature. Data were collected with a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 297 K. Unit cell parameters were determined from least-squares refinement of setting angles of 2675 reflections ($I > 2\sigma(I)$) out of 7387 collected data with 2θ in the range $3.9 \leq 2\theta \leq 56.6°$. A summary of the crystallographic data and structure refinement parameters are given in table 1. Reflection data were recorded using the ω scan technique in the hkl range $-47 \leq h \leq 53$, $-12 \leq k \leq 10$, $-14 \leq l \leq 16$. Data were corrected for Lorentz polarization effects and for linear decay. Semi-empirical absorption corrections based on ψ-scans were applied. The structure was solved by the heavy atom method using SHELXS-97 [16] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically.

Table 1. Summarized crystallographic data for **3a**.

Empirical formula	$C_{20}H_{20}N_{14}Ni$
Formula weight	515.22
Temperature (K)	297 (2)
Crystal system	Orthorhombic
Space group	*Fdd2*
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.20$
Unit cell dimensions (Å, °)	
a	41.391(5)
b	9.0247(9)
c	12.3375(13)
β	90.00
V (Å)^3	4608.5(8)
Z	8
λ (Å)	0.71073
μ (Mo-Kα) (mm^{-1})	0.883
D_{Calcd} ($mg\,m^{-3}$)	1.485
Refine parameters	159
Reflection number total	7387
Reflection number collected	2675
$R_1^a[I > 2\sigma(I)]$	0.0467
wR_2^b	0.1143
Goodness of fit	0.852

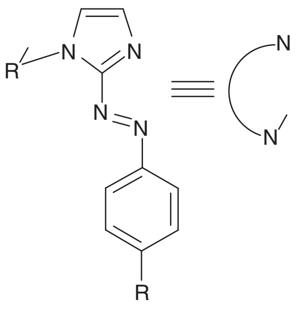
$^aR = \sum|F_o - F_c|/\sum F_o$; $^bwR = [\sum w(F_o^2 - F_c^2)/\sum wF_o^4]^{1/2}$ $w = 1/[\backslash\sigma^2\ (F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

The hydrogen atoms in aromatic rings and aliphatic groups were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual minima and maxima were −0.287 and 0.787 ($e\,\text{Å}^{-3}$), respectively; all calculations were carried out using SHELXL-97 [17], ORTEP-32 [18] and PLATON-99 [19] programs.

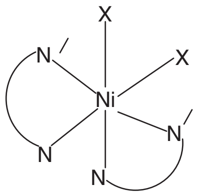
3. Results and discussion

3.1. *Synthesis and formulation*

Four ligands, 1-methyl-2-(phenylazo)imidazole (Pai-Me, **1a**), 1-ethyl-2-(phenylazo) imidazole (Pai-Et, **2a**), 1-methyl-2-(*p*-tolylazo)imidazole (Tai-Me, **1b**), 1-ethyl-2-(*p*-tollylazo)imidazole (Tai-Et, **2b**), have been used as N(imidazole) (N) and N(azo) (N$'$) bidentate chelating agents in the present work. Azide (N_3^-) and thiocyanate (SCN^-) are employed to balance charge of the complexes. The versatility of azido ligand (N_3^-), monodentate, μ-(1) [20], 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, is well established [21–26]. To a methanolic solution of $Ni(ClO_4)_2$ and RaaiR$'$in 1 : 2 mole ratio was added NaN_3 or NH_4SCN (2 equivalent) in MeOH. Solution color immediately turned to brown red, and brown black precipitate slowly separated on evaporation. The product was isolated in yields of >50%. The composition [Ni(RaaiR$'$)$_2$(X)$_2$] (**3**–**6**) was supported by microanalytical data. In an earlier report [14b] we isolated nickel(II) complexes, [Ni(RaaiR$'$)(H_2O)$_2$(X)$_2$].



RaaiR$'$ (**1**, **2**)



[Ni(RaaiR$'$)$_2$(X)$_2$]

[Ni(Pai-Me)$_2$(N_3)$_2$], **3a**; [Ni(Pai-Et)$_2$(N_3)$_2$], **4a**; [Ni(Tai-Me)$_2$(N_3)$_2$], **3b**; [Ni(Tai-Et)$_2$ (N_3)$_2$], **4b**; [Ni(Pai-Me)$_2$(SCN)$_2$], **5a**; [Ni(Pai-Et)$_2$(SCN)$_2$], **6a**; [Ni(Tai-Me)$_2$(SCN)$_2$], **5b**; [Ni(Tai-Et)$_2$(SCN)$_2$], **6b**.

The complexes are non-electrolytes in MeCN solution, and soluble in common organic solvents like $CHCl_3$ and CH_2Cl_2. Bulk room temperature magnetic moment with correction incorporating Pascal's diamagnetic constant show two electron paramagnetic nature of Ni(II) ($\mu_{av} = 2.6$–2.8 B.M.), suggesting a $t_{2g}{}^6e_g{}^2$ electronic configuration in octahedral geometry.

Pseudo-octahedral M(N,N$'$)$_2$X$_2$ exists in five stereoisomeric forms referring to coordination pairs of X,X; N,N; N$'$,N$'$; the isomers are abbreviated as *trans-cis-cis* (tcc); *trans-trans-trans* (ttt); *cis-trans-cis* (ctc); *cis-cis-trans* (cct) and *cis-cis-cis* (ccc). In Ru(II) complexes, Ru(N,N$'$)$_2$Cl$_2$, we have isolated four isomers [4] and two (*trans-cis-cis* (tcc) and *cis-trans-cis* (ctc)) were characterized by X-ray crystallographic study. [Co(N,N$^{/}$)$_2$(N$_3$)$_2$] exists as *cis-cis-cis* (*ccc*) isomer [14c], while [Cu(RaaiR$^{/}$)$_2$(X)$_2$] shows *cis-cis-trans* (*cct*) coordination sequence [14d].

3.2. *Molecular structure of [Ni(Pai-Me)$_2$(N$_3$)$_2$] (3a)*

Crystal structure of [Ni(Pai-Me)$_2$(N$_3$)$_2$] (**3a**) is shown in figure 1. Bond lengths and angles are listed in table 2. Ni(II) is coordinated by two Pai-Me and two azides to give *cis*-N,N (N refers to imidazole-N) and *trans*-N$^{/}$,N$^{/}$ (N$^{/}$ refers to azo-N) stereochemistry. Azide is a monodentate, μ-(1) donor. Two N_3^- groups coordinate *cis* around Ni(II).

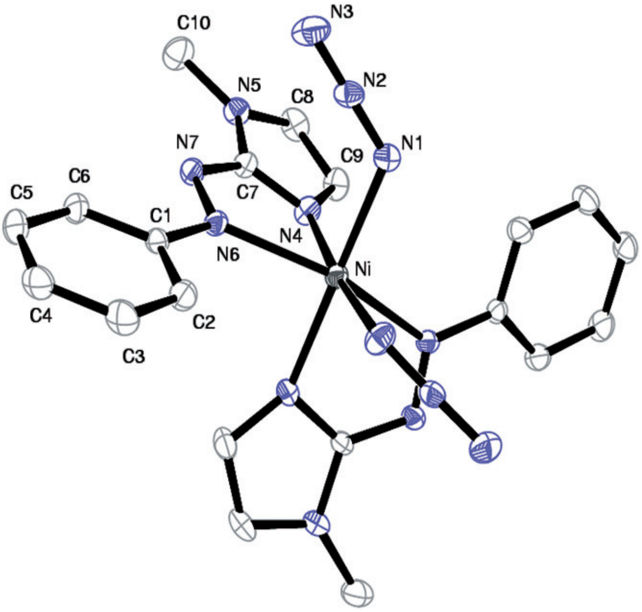


Figure 1. ORTEP of *cis-cis-trans*-[Ni(Pai-Me)$_2$(N$_3$)$_2$] (30% probability ellipsoid).

Table 2. Bond distances (Å) and angles (°) of **3a**.

Ni(1)–N(1)	2.097(3)	N(4)–Ni(1)–N(6)	75.99(11)
Ni(1)–N(4)	2.054(3)	N(1)–Ni(1)–N(4)	86.77(13)
Ni(1)–N(6)	2.216(3)	N(4)–Ni(1)–N(4)^{a}	99.11(19)
N(6)–N(7)	1.264(4)	N(4)–Ni(1)–N(6)^{a}	89.92(11)
N(1)–N(2)	1.171(4)	N(1)–Ni(1)–N(6)	89.08(12)
N(2)–N(3)	1.155(5)	N(1)–Ni(1)–N(1)^{a}	87.5(2)
N(7)–C(7)	1.378(4)	N(6)–Ni(1)–N(6)^{a}	158.06(15)
C(1)–N(6)	1.428(4)	N(4)–Ni(1)–N(1)^{a}	173.60(15)
		N(1)–Ni(1)–N(6)^{a}	106.92(12)

[a] Symmetry: $2-x$, $2-y$, z.

Thus, coordination sequence of azido-N, imidazole-N(N) and azo-N(N') describe *cis-cis-trans* (cct) orientation. The geometry is elongated octahedral with the equatorial plane formed by two imidazole nitrogens (each from individual ligand) and two azide-N donor centers. Two axial positions are occupied by two azo-N donor centers from two Pai-Me. The N–Ni–N'bond angle subtended by the chelating ligand is N(4)–Ni–N(6), 75.79(11)°. Other angles in the chelated motif also deviate in either direction from the regular five-member ring. The chelate ring constitutes a good plane (mean deviation ~0.03 Å). The pendant phenyl ring makes a dihedral angle 8.97(18)° with the chelate plane. The N(azo) requires considerably more room than the other two N-donors [27]. Two reasons are considered: (i) the N(azo) belongs to exocyclic N=N along with a pendant aryl group; thus the van der Waals repulsion will be greater than N(imidazole) and (ii) the N(azido) has larger s-character compared to N(azo) (because resonating N_3^- shows sp hybridized-N due to $^-N{=}N^+{=}N^- \leftrightarrow N{\equiv}N^+{-}N^-$ etc., while N=N in azo carries sp^2 hybridization) and thus N(azo) is more space demanding. The lowering of symmetry is manifested by elongation of axial bonds of the two N(azo) donor centers. The Ni–N(azo) distance, 2.216(3) Å, is less than the sum of the van der Waals radii of Ni(II) (1.63 Å) and N(azo) (1.55 Å) [27] and even less than previously reported Ni–N(azo) distance (2.252(3) Å) of $[Ni(MeaaiMe)(NCS)_2(H_2O)_2] \cdot 2DMF$ [14b], implying covalent interaction of N(azo) and Ni(II).

In the equatorial plane the *trans* angles are 173.60(15)° [N(1)–Ni(1)–N(4)]. The axial ∠N(6)–Ni(1)–N(6) is 158.06(15)°. The large deviation (~22°) from the *trans* angle (180°) is undoubtedly from the combined contribution of short chelate angle and steric requirement of azo-N centers. The azo, N=N, distance is 1.264(4) Å, which is longer than the free ligand value (1.250(1) Å) [8]. A small extension of azo bond may be due to structural strain arising from the small chelate bite angle and steric requirement of the chelated azoimine fragment.

Noncovalent bonding is also observed in this structure as C–H---π and C–H---N(azide) interactions. Phenyl C–H of one of the pendant rings interacts with imidazole ring of a neighboring molecule (figure 2): C(2)–H(2) ⋯ Cg1, 3.3491 Å (Cg1=N(4)–C(7)–N(5)–C(8)–C(9); symmetry = x, $1/2+y$, $1/2+z$); the C–H of $N{-}CH_3$ in imidazole of one molecule interacts with phenyl ring of adjacent molecule: C10–H10C ⋯ Cg2(#5.1), 3.2564 Å, (Cg2: C(1)–C(2)–C(3)–C(4)–C(5)–C(6); symmetry = $x, -1/2+y, -1/2+z$) generating a dimer. These two interactions appear alternately in the network. The C–H---N(azide) interactions are as follows: C(2)–H(2) ⋯ N(1)(Intra) (H(2) ⋯ N(1), 2.40 Å; C(2)–N(1), 3.282(7) Å; ∠C(2)–H(2) ⋯ N(1), 158° and symmetry, $-x, 1-y, z$), C(4)–H(4) ⋯ N(3) (H(4) ⋯ N(3), 2.55 Å; C(4)–N(3), 3.411(3) Å; ∠C(4)–H(4)–N3, 154° and symmetry, $x, 1+y, z$), C(8)–H(8)–N(3) (H(8)–N(3), 2.58 Å; C(8)–N(3), 3.479(9) Å; ∠C(8)–H(8)–N(3), 164° and symmetry, $x, -1/2+y, -1/2+z$).

3.3. *Spectral studies*

$[Ni(RaaiR')_2(N_3)_2]$ show characteristic strong absorptions at 2031–2039 cm^{-1} with a weak band at 2045–2047 cm^{-1} in infrared spectra, corresponding to $\nu_{asym}(N_3)$ [14a, 20, 21] with monodentate N_3^- in **3** and **4.** The $[Ni(RaaiR')_2(SCN)_2]$ (**5** and **6**) complexes show characteristic strong absorptions at

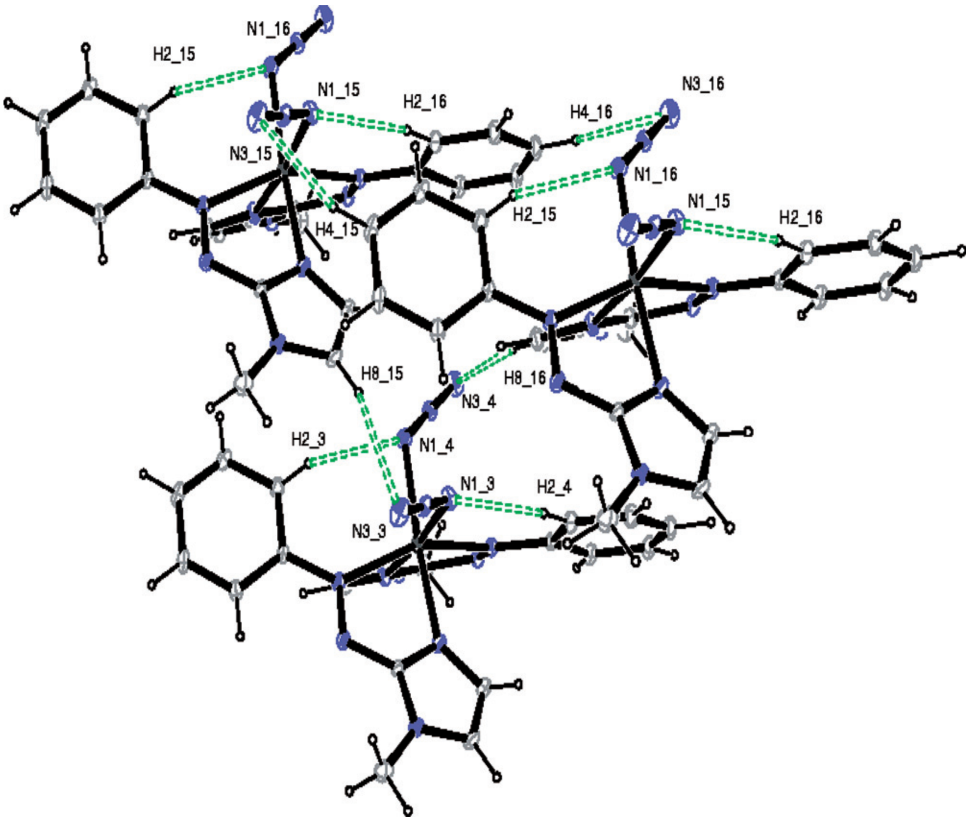


Figure 2. C–H ··· N(azide) interactions to generate a supramolecular network.

2098–2105 $\mathrm{cm^{-1}}$ with a weak band at 2090–2093 corresponding to ν(CN) of bound SCN. Medium to strong bands at 760–770 and 680–695 $\mathrm{cm^{-1}}$ have been assigned to ν(CS) for $[\mathrm{Ni(RaaiR^{/})_2(SCN)_2}]$. The ν(SCN) are at 450–470 and 400–420 $\mathrm{cm^{-1}}$. The ligand, $\mathrm{RaaiR^{/}}$, shows characteristic absorptions at 1600–400 $\mathrm{cm^{-1}}$. Moderately intense stretching at 1585–1600 and 1435–1440 $\mathrm{cm^{-1}}$ are due to ν(C=N) and ν(N=N), respectively.

The solution UV–Vis spectra were recorded in MeCN and data are listed in table 3. The absorption spectra of free ligands show absorption around 350–370 nm with a molar absorption coefficient on the order of $10^4\ \mathrm{M^{-1}\,cm^{-1}}$ and a tail extending into 400–420 nm (figure 3). From analogy with absorption spectra of azobenzene derivatives, the large absorption band around 400 nm corresponds to $\pi \rightarrow \pi^*$ transitions, while the tail corresponds to a $n \rightarrow \pi^*$ transition. The assignment is also supported by theoretical calculations [6]. These bands shift to longer wavelength on complexation. Intense bands ($\varepsilon \sim 10^4\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) in the range 430–445 nm may be assigned to $\mathrm{d}\pi(\mathrm{Ni}) \rightarrow \pi^*$(ligand) charge transfer transitions (figure 3). Two broad bands at longer wavelengths (710–720 and 630–635 nm) are observed and molar extinction coefficient data indicate admixture of d–d and MLCT transitions. The azoimine (–N=N–C=N–) is π-acidic enough to have MLCT transitions.

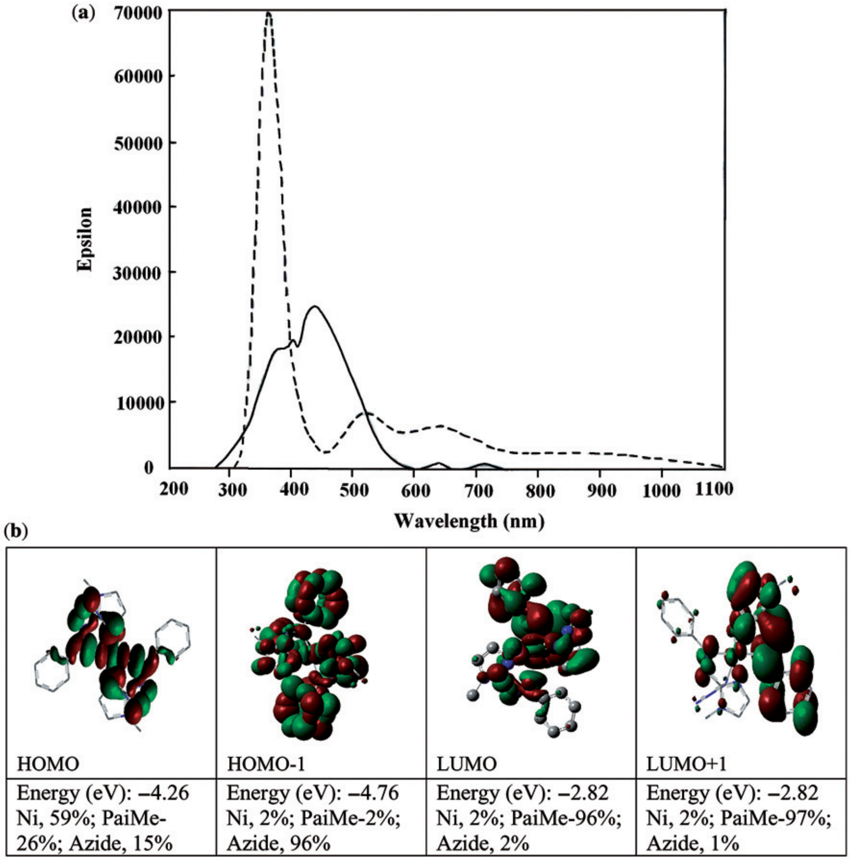
Table 3. UV–Vis[a], IR spectral and cyclic voltammetric data.

Compound	UV–Vis spectral data (λ_{max}/nm) ($10^{-3}\,\varepsilon\,M^{-1}\,cm^{-1}$)	IR data (KBr disk), cm^{-1} (N_3)/(SCN)(C=N)(N=N)			Cyclic voltammetric data[b] V (ΔE_p, mV) E_M E_L (ligand reductions)			
[Ni(Pai-Me)$_2$(N$_3$)$_2$] (**3a**)	382(1.86), 403(1.92), 440(2.55),633(0.18), 710(0.14)	2060	1582	1401	0.65	−0.14 (130)	−0.42 (160)	−1.04[c]
[Ni(Pai-Et)$_2$(N$_3$)$_2$] (**4a**)	382(2.13), 434(1.61), 445(2.42),630(0.11), 714(0.08)	2065	1580	1408	0.60	−0.17 (140)	−0.48 (150)	−0.95[c]
[Ni(Tai-Me)$_2$(N$_3$)$_2$] (**3b**)	382(3.49), 424(3.47), 446(2.86),635(0.16), 735(0.06)	2060	1588	1404	0.57	−0.16 (120)	−0.54 (140)	−1.02[c]
[Ni(Tai-Et)$_2$(N$_3$] (**4b**)	381(2.02), 424(2.13), 447(1.59),635(0.18), 738(0.06)	2064	1585	1416	0.64	−0.15 (130)	−0.58 (150)	−1.05[c]
[Ni(Pai-Me)$_2$(SCN)$_2$] (**5a**)	382(2.23), 393(1.84), 424(1.54),640(0.11), 734(0.07)	2082	1590	1415	0.73	−0.20 (130)	−0.56 (140)	−1.20[c]
[Ni(Pai-Et)$_2$(SCN)$_2$] (**5b**)	384(2.47), 394(2.01), 426(1.69),635(0.13), 730(0.04)	2080	1595	1412	0.75	−0.25 (140)	−0.60 (150)	−1.30[c]
[Ni(Tai-Me)$_2$(SCN)$_2$] (**6a**)	382(1.20), 409(1.29), 435(1.75),625(0.13), 728(0.06)	2081	1590	1418	0.70	−0.23 (120)	−0.60 (140)	−1.20[c]
[Ni(Tai-Et)$_2$(SCN)$_2$] (**6b**)	381(1.56), 411(1.65), 432(1.80),635(0.11), 710(0.06)	2090	1588	1417	0.76	−0.25 (130)	−0.64 (150)	−1.25[c]

[a] Solvent: Dichloromethane.

[b] Solvent: Acetonitrile, Pt-disk working electrode, reference SCE, supporting electrolyte [nBu$_4$N][ClO$_4$], $E_{1/2} = 0.5(E_{pa} + E_{pc})$, V; $\Delta E_p = |E_{pa} - E_{pc}|$, mV; E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential.

[c] E_{pc}; E_M = Ni(III)/Ni(II) irreversible wave. E_L = ligand reductions.



HOMO	HOMO-1	LUMO	LUMO+1
Energy (eV): −4.26 Ni, 59%; PaiMe-26%; Azide, 15%	Energy (eV): −4.76 Ni, 2%; PaiMe-2%; Azide, 96%	Energy (eV): −2.82 Ni, 2%; PaiMe-96%; Azide, 2%	Energy (eV): −2.82 Ni, 2%; PaiMe-97%; Azide, 1%

Figure 3. UV–Visible spectra of [Ni(Pai-Me)$_2$(N$_3$)$_2$] in acetonitrile, experimental (—) and theoretical (- - -). Drawings of HOMO, HOMO-1, LUMO and LUMO + 1.

DFT and TD-DFT analyses show that HOMO of [Ni(Pai-Me)$_2$(N$_3$)$_2$] (**3a**) carries 59% Ni orbitals, 26% Pai-Me and 15% azido contribution (figure 3). The LUMO (L) has 96% Pai-Me contribution with insignificant azido function. Some of the occupied molecular orbitals (HOMO-1, HOMO-2, HOMO-3, HOMO-4) contain high contribution of azide (>60%). Energies and compositions of molecular orbitals are given in supplementary table 1. The calculated spectral data (table 4) in MeCN reveal transitions centered at 380, 430, 630 and 725 nm. The calculated transitions of **3a**, HOMO → LUMO/LUMO + 1 (1.44 eV, 861 nm), H-1 → LUMO/LUMO + 1 (1.94 eV, 639 nm), H → LUMO + 2 (2.22 eV, 558 nm), H-2 → LUMO/LUMO + 1 (2.2 eV, 536 nm), H-3 → LUMO/LUMO + 1 (2.44 eV, 508 nm), H-4 → LUMO/LUMO + 1 (2.58 eV, 480 nm), H → LUMO + 3 (3.93 eV, 315 nm), are close to the experimental (table 3, figure 3). The transitions are mixed transitions like MLCT, LLCT or XLCT as given in table 4.

3.4. *Cyclic voltammetry*

Voltammetric data are in table 3 and a representative figure is shown in figure 4. During voltammetric experiments, the anodic current increases above 0.5 V and an anodic response

Table 4. Calculated transitions of **3a**.

λ, nm ($f \times 10^3$)	Transitions
645.3(0.0808)	(37%) H-2 → L + 2(XMCT), (13%)H-1 → L + 2(XMCT)
519.3(0.0723)	(61%)H-4 → LUMO(XLCT), (13%)H-6 → LUMO(MLCT)
514.2(0.0364)	(51%)H-4 → L + 2(XMCT), (27%)H-4 → LUMO(XLCT), (19%)H-2 → L + 2(XMCT)
410.5(0.0144)	(43%)HOMO → L + 9(d–d), (38%)HOMO → L + 7(MLCT), (27%)H-7 → L + 2(LMCT)
382.1(0.0563)	(56%)H-1 → L + 5(XLCT), (11%)H-1 → L + 8(XLCT)
375.8(0.0447)	(63%)HOMO → L + 10(d–d), (14%)H-6 → LUMO(MLCT), (11%)H-8 → L + 1(ILCT)
370.7(0.2697)	(41%)H-8 → L + 1(ILCT), (18%)H-6 → LUMO(MLCT)
364.7(0.0663)	(30%)H-6 → L + 1(MLCT), (28%)H-2 → L + 6(XLCT)
360.5(0.1677)	(44%)H-1 → L + 6(XLCT), (21%)H-2 → L + 7(XLCT), (15%)H-5 → L + 1(MLCT)
352.5(0.4254)	(36%)H-6 → L + 6(MLCT), (29%)H-6 → LUMO(MLCT), (16%)H-1 → L + 8(XLCT)

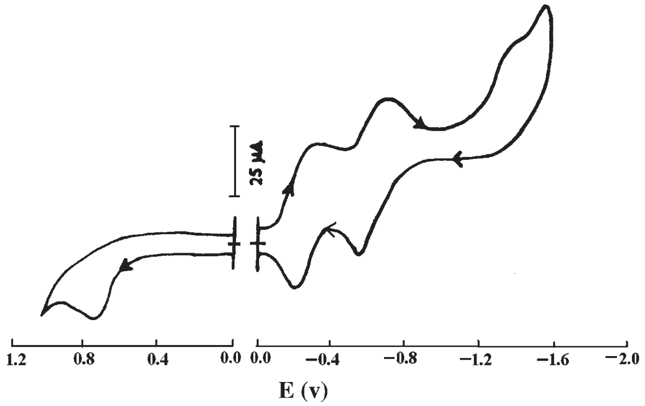


Figure 4. Cyclic voltammogram of [Ni(Pai-Et)$_2$(SCN)$_2$] (**5b**) in MeCN using Pt working electrode, SCE reference and [nBu$_4$N][ClO$_4$] supporting electrolyte.

is observed in the potential range 0.6–0.7 V, but no cathodic counterpart is observed on scan reversal. The anodic response may be assigned to very unstable Ni(III) species. Redox couples negative to SCE are reductive in nature and have been assigned to reductions of chelated azo-ligand. Arylazoheterocycles accommodate two electrons in the LUMO which is mostly azo in character: [–N=N]/[–N–N–]$^-$ and [–N–N]$^-$/[–N–N–]$^=$. The DFT calculation suggests 59% contribution of Ni(II) orbitals to HOMO, thus the anodic response may be referred to Ni(II) → Ni(III) [28]. The LUMO is basically RaaiR$'$oribtals, and thus the reduction is explained as electron feeding into the azo-dominated LUMO.

4. Conclusion

Nickel(II) forms *bis*-chelated azido/thiocyanato complexes of composition Ni(RaaiR$'$)$_2$(X)$_2$ (X=N$_3$, SCN) using metal:ligand:anion in the molar ratio of 1 : 2 : 2. The structure supports this composition. Solution spectra show mixed electronic transitions of MLCT, LLCT, XLCT type. Redox of the complexes show irreversible Ni(III)/Ni(II) couple along with ligand reduction. The electronic configuration, spectra and redox properties are supported by DFT and TD-DFT calculations.

Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 654228 for [Ni(Pai-Me)$_2$(N$_3$)$_2$]. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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