

Available online at www.sciencedirect.com



Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 842 (2007) 17-23

www.elsevier.com/locate/molstruc

# Manganese(II)-azido/thiocyanato complexes of naphthylazoimidazoles: X-ray structures of $Mn(\beta-NaiEt)_2(X)_2$ ( $\beta$ -NaiEt = 1-ethyl-2-(naphthyl- $\beta$ -azo)imidazole; X = N<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>)

D. Das <sup>a</sup>, B.G. Chand <sup>a</sup>, J.S. Wu <sup>b</sup>, T.-H. Lu <sup>b</sup>, C. Sinha <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700 032, India <sup>b</sup> Department of Physics, National Tsing Hua University, Hsinchu 300, Taiwan, ROC

Received 5 May 2006; received in revised form 29 November 2006; accepted 30 November 2006 Available online 24 January 2007

## Abstract

Manganese(II)-naphthylazoimidazole complexes using  $N_3^-$  and NCS<sup>-</sup> as counter ions are characterized as  $Mn(\beta-NaiR)_2(X)_2(\beta-Nai-Et = 1-alkyl-2-(naphthyl-\beta-azo)imidazole; <math>X = N_3^-$ , NCS<sup>-</sup>). The ligands are unsymmetric N(imidazole), N(azo) chelating agents. The microanalytical, spectral (FT-IR, UV-vis), magnetic (bulk moment and EPR) and electrochemical data establish the structure and composition of the complexes. The single crystal X-ray diffraction studies of  $Mn(\beta-NaiEt)_2(N_3)_2$  and  $Mn(\beta-NaiEt)_2(NCS)_2(\beta-NaiEt = 1-ethyl-2-(naphthyl-\beta-azo)imidazole)$  have confirmed the three dimensional structure of the complexes. Cyclic voltammetry exhibits high potential Mn(III)/Mn(II) couple along with azo reductions. The EPR spectra show usual pattern. © 2006 Elsevier B.V. All rights reserved.

Keywords: Naphthylazoimidazoles; Manganese(II); Azide; Thiocyanate; X-ray structure; Electrochemistry

## 1. Introduction

Imidazole is ubiquitous in biology and chemistry. It is therefore of interest to synthesize ligands containing imidazole and related heterocyclic system [1-3] Ar—N=N<sup>+</sup> is attached to imidazole backbone and has synthesized 2-(arylazo)imidazole (1) [4–9]. These ligands are endowed with  $\pi$ -acidic azoimine (—N=N—C=N—) function. The  $\pi$ -acidity is largely dependent on the nature of heterocycle, ring size, number of heteroatoms and substituents in the phenyl group [10]. In manganese(II)-azido complexes of 1-ethyl-2-(*p*-tolylazo)imidazole (1), N<sub>3</sub><sup>-</sup> acts as end-on and end-to-end bridger and forms 1D chain. The complex exhibits interesting local ferromagnetic, global antiferromagnetic coupling [11]. This has encouraged us to synthesize Mn(II) complexes with different types of ligands. In this work we are going to report Mn(II)-azido/thiocyanato complexes of 1-alkyl-2-(naphthyl- $\beta$ -azo)imidazole,  $\beta$ -NaiR (2) (Scheme 1, 2). The replacement of phenyl group by naphthyl group has increased the steric crowding and electron density on the active function [12]. Detail structural, magnetic and spectroscopic studies are reported hereunder (Scheme 1).

# 2. Results and discussion

#### 2.1. Synthesis and formulation

The reaction of  $\beta$ -NaiR (2), Mn(ClO<sub>4</sub>)<sub>2</sub>,6H<sub>2</sub>O and NaN<sub>3</sub>/NH<sub>4</sub>CNS using different ligand:metal:azide/thiocyanate ratio (1:1:2, 2:1:2, 3:2:4) in methanol solution has isolated complexes of identical composition of [Mn( $\beta$ -NaiR)<sub>2</sub>(X)<sub>2</sub>] (X = N<sub>3</sub><sup>-</sup> (3) and NCS<sup>-</sup> (4))irrespective of the stoichiometry of the reactants. The ligand has unsymmetric N donor centres: N(imidazole) and N(azo) refer to N and N', respectively. The composition of the complexes has been determined by microanalysis (C, H, N) (*vide* 

<sup>\*</sup> Corresponding author. Tel.: +91 9830632450; fax: +91 33 24146584. *E-mail address:* c\_r\_sinha@yahoo.com (C. Sinha).

<sup>0022-2860/\$ -</sup> see front matter @ 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2006.11.076



Scheme 1. MeaaiEt (1);  $\beta$ -NaiR (2). R = Me (a), Et (b), CH<sub>2</sub>Ph (c).

Section 3) and spectroscopic studies. The molar conductance measurement shows non-electrolytic nature of the complexes in MeCN. Single crystal X-ray structure determination confirms the structure and bonding in these complexes.

### 2.2. Molecular structures

The structures of  $[Mn(\beta-NaiEt)_2(N_3)_2]$  (3b) and  $[Mn(\beta-NaiEt)_2(N_3)_2]$ NaiEt)<sub>2</sub> (NCS) <sub>2</sub>] (4b) are shown in Figs. 1 and 2. Selected bond distances and angles are listed in Table 1. Each complex consists of a central manganese atom surrounded by two  $\beta$ -NaiEt ligands and two N donor centres from N<sub>3</sub><sup>-</sup> or NCS<sup>-</sup>. Thus MnN<sub>6</sub> distorted octahedral coordination environment is ensured. The two structures are essentially isostructural, both chemically and crystallographically. Pseudooctahedral complexes  $M(N,N')_2(X)_2$  may exist in five different isomeric forms: two of them will carry trans- $M(X)_2$  and three of them have *cis*- $M(X)_2$  motif [4]. The structures in Figs. 1 and 2 reveal cis-trans-cis arrangement in the sequence of  $cis-M(X)_2$ , trans-M(N(imidazole))<sub>2</sub> and  $cis-M(N(azo))_2$ . The structural distortion may be originated from large steric interaction between crowded naphthyl groups and low chelate angle [N(imidazole)-Mn-N(azo):



Fig. 1. Molecular structure of  $[Mn(\beta-NaiEt)_2(N_3)_2]$  (3b).



Fig. 2. Molecular structure of  $[Mn(\beta-NaiEt)_2(NCS)_2]$  (4b).

 $(65.78(5)^{\circ} (\mathbf{3b}) \text{ and } 66.62(9)^{\circ} (\mathbf{4b})]$ . The effect is significantly visible in case of Mn-N(azo) bond distance (Mn-N(1), 2.6571(16) Å for **3b** and Mn–N(1), 2.604(4) Å for **4b**) compared to Mn-N(imidazole) length (Mn-N(4) 2.1776(16) Å for **3b** and Mn-N(4), 2.179(3) Å for **4b**. Although Mn–N(azo) distances are very long but they are well below the sum of van der Waals radii of Mn(II) and N(azo) [11]. The azo distance (N(1)-N(2)), 1.2742(19) Å for 3b and 1.271(3) Å for 4b) is slightly elongated than free ligand value (1.266(3) Å [13]). The bond parameters are compared with reported data in [Mn(MeaaiEt)(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (Mn-N(imidazole), 2.221(2); Mn-N(azo), 2.562(2); N=N, 1.267(3) Å) [11]. The C(imidazole)–N(azo) length (C(1)–N(2), 1.390(2) Å for 3b/C(1)–N(2), 1.396(3) Å for 4b) is shorter than N(azo)-C(naphthyl) distance (N(1)-C(6), 1.417(2) Å for **3b** and 1.430(3) Å for **4b**). This is in support of the stronger interaction of azo-N with imidazole ring comparing with naphthyl group. The Mn-N(azide), Mn - N(5), is 2.092(2) Å while Mn - N(NCS)distance (Mn-N(5)) is 2.104(3) Å. The distances and angles with  $N_3^-$  and NCS<sup>-</sup> in the complexes are comparable with reported data [14-16] All other bond parameters lie within the limit of estimated deviation of free ligands [13].

The C–H– $\pi$  and  $\pi$ – $\pi$  interactions present in these structures. In **3b** azido-N, azo-N and imidazole/naphthyl  $\pi$ -rings act as acceptor and imidazole—C(2)—H(2), C(4)—H(4b) of N-Et group and C(7)-H(7) of naphthyl serve as H donor centres. Intermolecular hydrogen bonding is exhibited by azido-N (N(7)) of one molecule with imidazole C(2)-H(2) of neighbouring molecule  $[C(2)-H(2)-N(7)^*: H(2)-N(7),$ 2.53 Å, C(2)–N(7), 3.362(1) Å,  $\angle$ C(2)–H(2)–N(7), 149<sup>0</sup>; \*symmetry: 1 - x, 1 - y, 1 - z]. The C–H– $\pi$  and  $\pi$ - $\pi$  interactions enhance the robustness of the molecule. The observed C-H- $\pi$  interactions are C(7)-H(7)-Cg(1) [H(7)-Cg(1), 2.840(8) Å; symmetry, 1 - x, y, 1/2 - z],C(4)-H(4b)-Cg(3) [H(4b)-Cg(3), 3.320(6) Å; symmetry, 1 - x, y, 1/2 - z]. The  $\pi$ - $\pi$  interaction is weak: Cg(1)-Cg(2) (4.288(4) Å), (where Cg(1): N(4)-C(1)-N(3)-C(2)-C(3); Cg(2): C(6)-C(7)-C(8)-C(13)-C(14)-C(15); symmetry, 1 - x, y, 1/2 - z) and provides interchain rigidity to the

	$\sim$
	~7
	~
•	~

	Bond distances (Å)		<u> </u>	Bond angles (°)	
	3b	4b		3b	4b
Mn-N(1)	2.6571(16)	2.604(4)	N(1) - Mn(1) - N(4)	65.78(5)	66.62(9)
Mn-N(4)	2.1776(16)	2.179(3)	N(1)-Mn(1)-N(5)	96.56(7)	99.18(10)
Mn - N(5)	2.092(2)	2.104(3)	N(5)— $Mn$ — $N(4)$	111.41(7)	107.81(11)
N(1) - N(2)	1.2742(19)	1.271(3)	$N(5^{a})$ — $Mn$ — $N(4)$	90.62(7)	92.89(11)
N(5) - N(6)	1.138(2)		$N(5)$ — $Mn$ — $N(5^a)$	101.42(12)	95.34(17)
N(6) - N(7)	1.183(3)		$N(4)$ — $Mn$ — $N(4^a)$	145.47(9)	149.33(14)
N(5)-C(16)		1.157(4)	$N(4^a)$ — $Mn$ — $N(1)$	86.21(5)	88.32(9)
C(16)—S		1.614(4)	$N(5^{a})$ — $Mn$ — $N(1)$	154.44(7)	157.72(11)
C(1) - N(2)	1.390(2)	1.396(3)	N(5) - N(6) - N(7)	176.2(2)	
C(6) - N(1)	1.417(2)	1.430(3)	N(5)-C(16)-S		178.1(4)

Table 1 Selected bond distances (Å) and bond angles (°) for  $[Mn(\beta-NaiE1),(N_2),]$  (**3b**) and  $[Mn(\beta-NaiE1),(NCS),]$  (**4b**)

<sup>a</sup> Symmetry: -x, y, 3/2 - z for **3b** and -x, y, 1/2 - z for **4b**.

solid state geometry (Fig. 3). The noncovalent interactions in  $[Mn(\beta-NaiEt)_2(NCS)_2]$  (4b) are the C-H-Cg interactions (Fig. 4) [C(7)-H(7)-Cg(1), 2.907(2) Å; C(5)-H(5b)-Cg(3), 3.127(6) Å] and weak  $\pi-\pi$  interactions [Cg(1)-Cg(2), 4.272(5) Å; Cg(1)-Cg(3), 4.348(1) Å where Cg(1), N(3)-C(11)-N(4)-C(13)-C(12); Cg(2), C(1)-C(2)-C(3)-C(8)-C(9)-C(10); Cg(3), C(3)-C(4)-C(5)-C(6)-C(7)-C(8); symmetry: <math>1/2 - x, 1/2 - y, 1 - z].

# 2.3. Spectral studies

Infrared spectra of  $[Mn(\beta-NaiR)_2(N_3)_2]$  (3) show very sharp strong stretch at 2045–2055 cm<sup>-1</sup> and is assigned to  $v(N_3)$ . In  $[Mn(\beta-NaiR)_2(NCS)_2]$  (4) the v(NCS) appears at 2065–2080 cm<sup>-1</sup>. Moderately intense stretchings at 1580– 1590 and 1400–1410 cm<sup>-1</sup> are due to v(C=N) and v(N=N), respectively. Solution electronic spectra of the complexes show intense transition <400 nm and are due to ligand centered transitions. A broad band (Table 2;  $\varepsilon \sim$  $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) at  $\geq$ 440 nm may be referred to the combination of MLCT and d–d transitions. The spectral profile is in support of Oh–Mn(II) stereochemistry [17].

## 2.4. Magnetic moment and EPR spectra

The magnetic moment,  $\mu_{\text{eff}}$  is av. 5.2–5.5 BM at 300 K expected for an isolated S = 5/2 Mn(II) monomer [18]. The EPR spectra of a solution in MeCN at 77 K display  $g \approx 2$ ,  $m_{\text{s}} = +1/2$  to -1/2 fine structure transition split into six hyperfine lines as expected for <sup>55</sup>Mn(II) complex (I = 5/2) along with superfine splitting (Fig. 5). A notable feature of the spectra is the relatively low value of the hyperfine coupling constant A, 80–90 G. Each hyperfine shows doublet splitting at 77 K which suggests interaction of ligand–N with Mn(II).

## 2.5. Electrochemistry

Redox properties of the manganese complexes have been studied by cyclic voltammetry (CV) using a platinum working electrode. Voltammogram data are collected in

![](_page_2_Figure_13.jpeg)

Fig. 3.  $\pi$ - $\pi$  interaction incorporates supramolecularity to the molecule 3b.

![](_page_3_Figure_1.jpeg)

Fig. 4.  $\pi$ - $\pi$  interaction incorporates supramolecularity to the molecule 4b.

Table 2 and representative diagram is shown in Fig. 6. A couple appears at 0.80–1.1 V *versus* SCE is referred to Mn(III)/Mn(II) redox process [19]. The quasireversibility of the process is examined from peak-to-peak separation,  $\Delta Ep > 100$  mV. One electron nature of the redox process has been confirmed by DPV studies. Ligand reductions are irreversible in nature and the Ep<sub>c</sub> values are compara-

Table 2 UV–vis spectra<sup>a</sup>, cyclic voltammetric<sup>b</sup> and magnetic moment ( $\mu$ ) data

ble with free ligand values [20]. The reduction is attributed to the electron accommodation to azo-dominated orbitals.

# 3. Experimental

## 3.1. Materials

Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was prepared by adding MnCO<sub>3</sub> to warm HClO<sub>4</sub> solution (1:1, v/v) and recrystallised from water in presence of few drops of HClO<sub>4</sub>. Sodium azide (SRL, India) were purchased from the market and used without further purification. 1-Alkyl-2-(naphthyl-βazo)imidazoles (β-NaiR (2)) were prepared by a reported procedure [13]. All other chemicals and solvents used for preparative and spectroscopic work of reagent grade and were used as received. Purification of MeCN [21] and preparation of [*n*-Bu<sub>4</sub>N][ClO<sub>4</sub>] were done following the method given in reference [20].

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

# 3.2. Physical measurements

IR spectra (KBr discs, 4000–400 cm<sup>-1</sup>) were recorded on a RX-1 Perkin-Elmer FTIR spectrophotometer. Microanalyses (C, H, and N) were done with a Perkin-Elmer 2400 CHNS/O elemental analyzer. The solution spectra were run at room temperature on Lambda 25 Perkin-Elmer spectrophotometer in the 200–900 nm range. Magnetic measurements were carried out in the vibrating sample magnetometer on polycrystalline samples working in room temperature (298 K). The diamagnetic corrections were evaluated from Pascal's constants. EPR spectra were recorded on powder samples at X-band frequency with a BRUKER 300E automatic spectrometer at room temperature (295 K) and 77 K. Electrochemical measurements were carried out with the use of computer controlled EG & G PARC VersaStat model 250 Electrochemical instrument

$(\mu)$ dua						
Compound	UV-vis spectral data $[\lambda_{max}(nm)]$ $(10^{-4} \varepsilon M^{-1} cm^{-1})$	Cyclic voltar	nmetric data (V),	Mn <sup>III</sup> / Mn <sup>II</sup> ligan	d reduction	μ (BM)
$[Mn(\beta-NaiMe)_2(N_3)_2] (3a)$	455 (0.87), 390 (0.665), 374 (0.754), 345 (0.778), 264 (1.020)	1.00 (100)	-0.45 (100)	-1.00 (140)	-1.35 <sup>c</sup>	5.32
$[Mn(\beta-NaiEt)_2(N_3)_2]$ (3b)	462 (1.13), 346 (0.75), 311 (0.63), 287 (1.14), 265 (1.91)	0.93 (120)	-0.48 (110)	-1.05 (130)	$-1.40^{\circ}$	5.24
$[Mn(\beta-NaiBz)_2 (N_3)_2] (3c)$	460 (1.28), 370 (1.54), 345 (1.77), 268 (1.520)	1.08 (120)	-0.40(130)	-0.95 (150)	-1.35 <sup>c</sup>	5.46
$[Mn(\beta-NaiMe)_2(NCS)_2]$ (4a)	433 (0.31), 386 (0.457), 265 (0.403)	0.87 (100)	-0.54(100)	-1.18(140)	$-1.41^{\circ}$	5.48
$[Mn(\beta-NaiEt)_2(NCS)_2]$ (4b)	440 (0.55), 380 (0.758), 265 (0.98)	0.80 (120)	-0.61(110)	-1.14 (135)	$-1.45^{\circ}$	5.52
$[Mn(\beta-NaiBz)_2(NCS)_2] (4c)$	450 (0.81), 396 (0.780), 275 (1.11)	0.92 (100)	-0.50 (100)	-1.10 (140)	$-1.40^{\circ}$	5.47

<sup>a</sup> Solvent, MeCN.

<sup>b</sup> Solvent, MeCN, Pt-disk working electrode; Pt-wire auxiliary and Ag/AgCl reference, [*n*-Bu<sub>4</sub>N][ClO<sub>4</sub>] supporting electrolyte, scan rate 50 mV s<sup>-1</sup>, potential  $E_{1/2} = (Ep_a + Ep_c)/2$  V;  $\Delta Ep = |Ep_a - Ep_c|$  mV.

<sup>c</sup> Ep<sub>c</sub>, V.

![](_page_4_Figure_1.jpeg)

Fig. 5. EPR spectra of  $[Mn(\beta-NaiMe)_2(N_3)_2]$  in MeCN solution at 77 K.

![](_page_4_Figure_3.jpeg)

Fig. 6. Cyclic voltammogram of  $[Mn(\beta-NaiEt)_2(N_3)_2]$  (3b) in MeCN.

using a Pt-disk working electrode and Pt-wire auxiliary electrode. The solution was IR compensated and the results were collected at 298 K. The reported results are referenced to Ag/AgCl in acetonitrile and are uncorrected for junction potential  $[n-Bu_4N]$ [ClO<sub>4</sub>] was used as supporting electrolyte.

## 3.3. Preparation of complexes

The complexes were prepared following three different ligand:metal:azide/thiocyanate stoichiometry, 1:1:2, 2:1:2, 3:2:4 in methanol under stirring condition using  $\beta$ -NaiMe as ligand. The compound isolated from these three inde-

pendent experiments were of same composition,  $[Mn(\beta-NaiEt)_2(X)_2)$ . Yield of the product is found highest in case of 2:1:2 ligand:metal:azide/thiocyanate. This method is described detail below.

To a methanolic solution  $(15 \text{ cm}^3)$  of 1-ethyl-2-(naphthyl- $\beta$ -azo)imidazole ( $\beta$ -NaiEt, 0.32 g, 1.28 mmol) was added dropwise to Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2 g, 0.56 mmol) in the same solvent (20 cm<sup>3</sup>) at room temperature (298 K). The mixture was stirred for 15 min and a small portion of yellow mass was filtered and rejected. To this filtrate NaN<sub>3</sub> (0.075 g, 1.15 mmol) in MeOH was added. The mixture was kept undisturbed for few days. Dark brown crystalline compound was filtered and washed with cold water and methanol and dried in vacuo over silicagel indicator. Yield: 0.2 g (60 %).

Elemental analyses were as follows: [Mn(β-Nai-Me)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] (**3a**),  $C_{28}H_{24}N_{14}Mn$ : calcd C, 55.00; H, 3.93; N, 32.08. Found : C, 54.88; H, 3.85; N, 32.00%. [Mn(β-NaiEt)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] (**3b**),  $C_{30}H_{28}N_{14}Mn$ : calcd C, 56.34; H, 4.38; N, 30.68. Found : C, 56.28; H, 4.32; N, 30.77%.[Mn(β-NaiBz)<sub>2</sub> (N<sub>3</sub>)<sub>2</sub>] (**3c**),  $C_{40}H_{32}N_{14}Mn$ : calcd C, 62.91; H, 4.19; N, 25.69. Found: C, 63.02; H, 4.12; N, 25.75%.

[Mn(β-NaiR')<sub>2</sub>(NCS)<sub>2</sub>] (**4**) were also synthesised following similar procedure using 2 equiv of NH<sub>4</sub>CNS in the reaction. The products were isolated in 65–70% yield. Elemental analyses were as follows. Mn(β-NaiMe)<sub>2</sub>(NCS)<sub>2</sub>] (**4a**), C<sub>30</sub>H<sub>24</sub>N<sub>10</sub>SMn: calcd C, 55.99; H, 3.73; N, 21.77. Found: C, 56.11; H, 3.80; N, 21.90%. [Mn(β-NaiEt)<sub>2</sub>(NCS)<sub>2</sub>] (**4b**), C<sub>32</sub>H<sub>28</sub>N<sub>10</sub>SMn: calcd C, 57.23; H, 4.17; N, 20.87. Found: C, 57.17; H, 4.22; N, 21.00%. [Mn(β-Nai-Bz)<sub>2</sub>(NCS)<sub>2</sub>] (**4c**), C<sub>42</sub>H<sub>32</sub>N<sub>10</sub>SMn: calcd C, 63.40; H, 4.03; N, 17.61. Found: C, 63.31; H, 4.10; N, 17.72%.

## 3.4. X-ray crystal structure determination of 3b and 4b

A crystal suitable for X-ray analysis was mounted on the Bruker SMART CCD area detector equipped with fine-focus sealed tube graphite monochromator and MoKa radiation ( $\lambda = 0.71073$  Å). Data were collected at 296(2) K for these complexes (Table 3). Red coloured blocked crystal size were  $0.2 \times 0.2 \times 0.1$  mm for **3b** and  $0.3 \times 0.2 \times 0.2$  mm for 4b. Unit cell parameters were determined from leastsquares refinement of setting angles with  $2\theta$  range 3.8– 56.7° for 3b and 3.84–56.6° for 4b. The hkl range were  $-25 \le h \le 13$ ,  $-18 \le k \le 18$ ,  $-16 \le l \le 17$  for **3b** and  $-25 \le h \le 23, -15 \le k \le 18, -16 \le l \le 19$  for **4b**. A summary of the crystallographic data and structure refinement parameters is given in Table 4. Of 10657 collected reflections 3781 unique reflection  $(I > 2\sigma(I))$  for **3b** and of 10785 collected data 3914 unique data for 4b were recorded using the  $\omega$ -scan technique. Data were corrected for Lorentz polarization effects and for linear decay. Semi-empirical absorption correction based on  $\psi$ -scans were applied. Data refinement and reduction were carried out by Bruker SMART and Bruker SAINT programme,

Table 3

Crystallographic data of  $[Mn(\beta\text{-}NaiEt)_2(N_3)_2]$  (3b) and  $[Mn(\beta\text{-}NaiEt)_2(NCS)_2]$  (4b)

	$\begin{array}{l} [Mn(\beta\text{-}NaiEt)_2(N_3)_2]\\ \textbf{(3b)} \end{array}$	$\begin{array}{l} [Mn(\beta\text{-}NaiEt)_2(NCS)_2] \\ \textbf{(4b)} \end{array}$
Empirical formula	$C_{30}H_{28}N_{14}Mn$	$C_{32}H_{28}N_{10}S_2Mn$
Formula weight	639.60	671.70
Temperature (K)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Crystal size (mm)	$0.20\times0.20\times0.10$	$0.30 \times 0.20 \times 0.20$
Unit cell dimensions		
a (Å)	19.2755(15)	19.8815(16)
b (Å)	13.9617(11)	13.9714(11)
<i>c</i> (Å)	13.4542(10)	14.2612(11)
β (°)	123.2430(10)	125.3960(10)
$V(\text{\AA})^3$	3028.2(4)	3229.2(4)
Ζ	8	8
$\lambda$ (Å)	0.71073	0.71073
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	0.483	0.578
$D_{\text{calcd}} (\text{mg m}^{-3})$	1.403	1.382
Refine parameters	204	204
Total reflections	10657	10785
Observed data $[I > 2\sigma$ (I)]	3761	3914
$\mathbf{R}_{1}^{a} [I \geq 2\sigma (I)]$	0.0431	0.0556
$wR_2^{\bar{b}}$	0.1118	0.1383
Goodness of fit	0.849	0.882

<sup>a</sup>  $\mathbf{R} = \Sigma |F_0 - F_c| / \Sigma F_0.$ 

<sup>b</sup>  $wR_2 = [\Sigma w (F_0^2 - F_c^2) / \Sigma w F_0^4]^{1/2}, \quad w = 1/[\sigma^2 (F_o^2) + (0.0635P)^2]$  (3b);  $w = 1/[\sigma^2 (F_o^2) + (0.7000P)^2]$  (4b) where  $P = (F_o^2 + 2F_c^2)/3$ . respectively. The structure was solved by direct method using SHELXS-97 [22] and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using riding model. In the final difference Fourier map the residual maxima and minima were 0.470 and  $-0.252 \text{ e} \text{ Å}^{-3}$  for **3b** and 0.273 and  $-0.247 \text{ e} \text{ Å}^{-3}$  for **4b**. All calculations were carried out using SHELXL-97 [23], ORTEP-32 [24], and PLA-TON-99 [25] programs.

## 4. Conclusion

We have synthesized Mn(II) complexes of 1-alkyl-2-(naphthyl- $\beta$ -azo)imidazoles with azide N<sub>3</sub><sup>-</sup> or thiocyanate (NCS<sup>-</sup>) as counter ion. Ligand serves as bidentate unsymmetric imidazole-N and azo-N chelator to synthesize high spin distorted octahedral [Mn( $\beta$ -NaiR')<sub>2</sub>(X)<sub>2</sub>] (X = N<sub>3</sub><sup>-</sup> (3 and NCS<sup>-</sup> (4); R' = Me (a) and Et (b)). The complexes are structurally characterized by single crystal X-ray diffraction studies. The stereochemistry is also supported by EPR spectra. Redox properties show high potential Mn(III)/Mn(II) couple and azo reductions.

# 5. Supplementary data

Crystallographic data for the structural analysis are in the Cambridge Crystallographic Data Centre, and CCDC No. 602420 for  $[Mn(\beta-NaiEt)_2(N_3)_2]$  (**3b**) and 601287 for  $[Mn(\beta-NaiEt)_2(NCS)_2]$  (**4b**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1FZ, UK (email:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

### Acknowledgement

Financial support from Department of Science and Technology, New Delhi is gratefully acknowledged.

# References

- [1] X.S. Tan, J. Sun, C.H. Hu, D.G. Fu, D.F. Xiang, P.J. Zheng, W.X. Tang, Inorg. Chim. Acta 257 (1997) 203.
- [2] L.E. Kapinos, B. Song, H. Sigel, Inorg. Chim. Acta. 280 (1998) 50.
- [3] C.J. Matthews, W. Clegg, S.L. Heath, N.C. Martin, M.N.S. Hull, J.C. Lockhart, Inorg. Chem. 37 (1998) 199.
- [4] T.K. Misra, D. Das, C. Sinha, P. Ghosh, C.K. Pal, Inorg. Chem. 37 (1998) 1672.
- [5] P. Byabartta, S.k. Jasimuddin, B.K. Ghosh, C. Sinha, A.M.Z. Slawin, J.D. Woollins, New J. Chem. 26 (2002) 1415.
- [6] J. Dinda, D. Das, P.K. Santra, C. Sinha, L.R. Falvello, J. Organomet. Chem. 629 (2001) 28.
- [7] S. Pal, D. Das, C. Sinha, C.H.L. Kennard, Inorg. Chim. Acta 313 (2001) 21.
- [8] U.S. Ray, B.G. Chand, G. Mostafa, J. Cheng, T.-H. Lu, C. Sinha, Polyhedron 22 (2003) 2587.
- [9] B.G. Chand, G. Mostafa, T.-H. Lu, L.R. Falvello, C. Sinha, Polyhedron 22 (2003) 3161.
- [10] E.C. Constable, Coord. Chem. Rev. 93 (1989) 205.

- [11] U.S. Ray, S.k. Jasimuddin, B.K. Ghosh, M. Monfort, J. Ribas, G. Mostafa, T.-H. Lu, C. Sinha, Eur. J. Inorg. Chem. (2004) 250.
- [12] L. Finar, sixth ed.Organic Chemistry, vol. 1, Longman, New York, 1971.
- [13] J. Dinda, K. Bag, C. Sinha, G. Mostafa, T.-H. Lu, Polyhedron 22 (2003) 1367.
- [14] J. Ribas, A. Escure, M. Monfort, R. Vicente, R. Cortes, L. Lezama, T. Rojo, Coord. Chem. Rev. 1027 (1999) 193–195, 1027.
- [15] M.A.S. Goher, J. Cano, Y. Journaux, M.A.M. Abu-Youssef, F.A. Mautner, A. Escure, R. Vicente, Chem. Eur. J. 6 (2000) 778.
- [16] S. Dalai, P.S. Mukherjee, T. Mallah, M.G.B. Drew, N.R. Chaudhuri, Inorg. Chem. Commun. 5 (2002) 472.
- [17] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier Science, Amsterdam, 1984.

- [18] R.L. Dutta, A. Syamal, Elements of Magnetochemistry, second ed., Affiliated East-West Press, New Delhi, 1993.
- [19] T. Mathur, U.S. Ray, J.-C. Liou, J.-S. Wu, T.-H. Lu, C. Sinha, Polyhedron 24 (2005) 739.
- [20] J. Dinda, Ph. D. Thesis, Burdwan University, Burdwan, India, 2003.
- [21] A.I. Vogel, A Text Book of Practical Organic Chemistry, second ed., Longman, London, 1959.
- [22] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Gottingen, Germany, 1997.
- [23] G.M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structure, University of Gottingen, Germany, 1997.
- [24] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
- [25] A.L. Spek, PLATON, Molecular Geometry Program, University of Utrecht, The Netherlands, 1999.