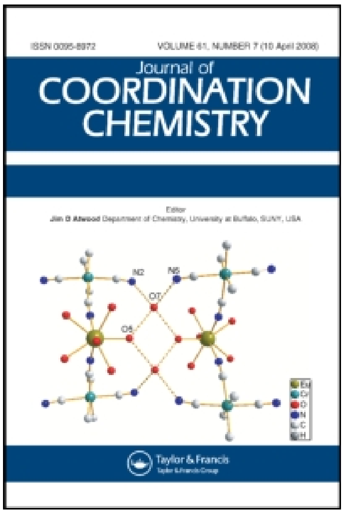

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M-NCO (M=Mn, Zn) complexes of 1-alkyl-2-(arylazo)imidazole: crystal structures of [Mn(MeaaiEt)$_2$(NCO)$_2$] and [Zn(HaaiMe)$_2$(NCO)$_2$] [HaaiMe=1-methyl-2-(phenylazo)imidazole and MeaaiEt=1-ethyl-2-(*P*-tolylazo)imidazole]

Umasankar Ray[a]; Debasis Banerjee[a]; Brojo Gopal Chand[a]; Jack Cheng[bc]; Tian-Huey Lu[c]; Chittaranjan Sinha[b]
[a] Department of Chemistry, The University of Burdwan, Burdwan 713 104, West Bengal, India [b] Department of Chemistry, Jadavpur University, Kolkata 700 032, West Bengal, India [c] Department of Physics, National Tsing-Hua University, Hsinchu 300, Taiwan, ROC

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M–NCO (M = Mn, Zn) complexes of 1-alkyl-2-(arylazo)imidazole: crystal structures of [Mn(MeaaiEt)$_2$(NCO)$_2$] and [Zn(HaaiMe)$_2$(NCO)$_2$] [HaaiMe = 1-methyl-2-(phenylazo)imidazole and MeaaiEt = 1-ethyl-2-(*P*-tolylazo)imidazole]

UMASANKAR RAY†, DEBASIS BANERJEE†, BROJO GOPAL CHAND†,
JACK CHENG‡§, TIAN-HUEY LU§ and CHITTARANJAN SINHA*‡

†Department of Chemistry, The University of Burdwan,
Burdwan 713 104, West Bengal, India
‡Department of Chemistry, Jadavpur University, Jadavpur,
Kolkata 700 032, West Bengal, India
§Department of Physics, National Tsing-Hua University,
Hsinchu 300, Taiwan, ROC

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Reaction of M(OAc)$_2\cdot$4H$_2$O (M = Mn, Zn) and 1-alkyl-2-(arylazo)imidazole [RaaiR′ where R = H (**a**), Me (**b**); R′ = Me (**1**/**3**/**5**), Et (**2**/**4**/**6**)] and NaNCO in methanol at 1 : 2 : 2 mol ratio gave [Mn(RaaiR′)$_2$(NCO)$_2$] (**3**, **4**) and [Zn(RaaiR′)$_2$(NCO)$_2$](**5**, **6**) complexes. The structures of these species were confirmed by single-crystal X-ray studies of **4b** and **5a**.

Keywords: Arylazoimidazoles; Manganese(II); Zinc(II); X-ray structures

1. Introduction

This work stems from our continued interest in the development of the transition metal chemistry of arylazoimidazoles [1–11]. The azoimine (–N=N–C=N–) group has two N donor centres and they differ in view of their hardness, π-acidity, and steric factors. X-ray structure studies of transition and non-transition metal complexes of arylazoimidazoles show that the azo-N prefer to bind to Ru(II) [1, 2], Os(II) [3], Pd(II) [4] and Pt(II) [5] while imidazole-N selectively binds the non-transition metals Zn(II), Cd(II) and Hg(II) [12–14], Ag(I) [11] and transition metals Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) [6–10]. In the presence of pseudohalides (N_3^-, NCS$^-$) as counter

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*Corresponding author. Email: c_r_sinha@yahoo.com

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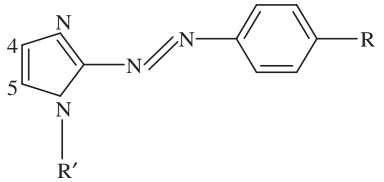
ions mononuclear [9, 10], dinuclear [8] and polynuclear complexes [6] of 3d metal ions have been obtained. Nuclearity and dimensionality of the complexes depend on composition, solvent, temperature and sequence of addition of components [8]. Use of NCO^- as a pseudohalide in the synthesis of the complexes is relatively less explored compared to N_3^- and NCS^-. In this work we describe Mn(II) and Zn(II) complexes of 1-alkyl-2-(arylazo)imidazoles (RaaiR′; below) using NCO^- as counter ion. Structures are supported by single-crystal X-ray studies of representative cases.



RaaiR′; R = H(**a**), Me(**b**); R′ = Me(**1**), Et(**2**)

2. Experimental

2.1. *Materials*

Published methods [1] were used to prepare 1-alkyl-2-(arylazo)imidazoles (RaaiR′ where R = H (**a**), Me (**b**) ; R′ = Me (**1**, **3**), Et (**2**, **4**)). All other chemicals and organic solvents used were of reagent grade.

2.2. *Physical measurements*

Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 CHNO/S instrument. Spectroscopic measurements were carried out using the following instruments: electronic spectra, Jasco V-570; IR spectra (KBr discs, 4000–200 cm^{-1}), Jasco 420 spectrophotometers. Room temperature magnetic moments were measured using a vibrating sample magnetometer at 298 K. Electrochemical measurements were carried out using a PAR 250 system and 270 software package. In cyclic voltammetry the following conditions were used: solvent, dry MeCN; supporting electrolyte, $[nBu_4N][ClO_4]$ ($\sim$0.1 M); solute concentration ($\sim 10^{-3}$ M); working electrode, Pt-disk electrode; reference electrode, SCE; auxiliary electrode, Pt-wire; scan rate, 50 $mV\,s^{-1}$; formal potential, $E^0 = 0.5(Ep_a + Ep_c)$ where Ep_a and Ep_c are anodic and cathodic peak potentials, respectively; ΔEp ($|Ep_a - Ep_c|$) is the peak-to-peak separation. ESR spectra were measured in MeCN solution at room (298 K) and liquid nitrogen (77 K) temperatures using a Bruker EMX 10/12 spectrometer operating at X-band frequencies and using an ER 4119 HS cylindrical resonator.

2.3. *$Mn(MeaaiEt)_2(NCO)_2$ (4b)*

A methanol solution (15 cm^3) of 1-ethyl-2-(*p*-tolylazo)imidazole (MeaaiEt, 0.34 g, 1.7 mmol) was added to $Mn(OAc)_2 \cdot 4H_2O$ (0.2 g, 0.82 mmol) in the same solvent (20 cm^3) at room temperature (298 K). An aqueous methanol solution of NaNCO (0.11 g, 1.7 mmol) was then added dropwise. The mixture was stirred for 15 min and filtered, and the filtrate kept undisturbed for a few days. Brown-red crystals were filtered off, washed with cold water and methanol, and dried *in vacuo*. Yield: 0.28 g (64%). All other Mn complexes were prepared by the same procedure and yields were 60–70%. [Mn(HaaiMe)$_2$(NCO)$_2$] (**3a**): Anal. Calcd for $C_{22}H_{20}N_{10}O_2Mn$ (%): C, 51.67; H, 3.91; N, 27.40. Found: C, 51.57; H, 3.85; N, 27.30. [Mn(MeaaiMe)$_2$ (NCO)$_2$] (**3b**): Anal. Calcd for $C_{24}H_{24}N_{10}O_2Mn$ (%): C, 53.43; H, 4.45; N, 25.97. Found: C, 53.49; H, 4.38; N, 25.90. [Mn(HaaiEt)$_2$(NCO)$_2$] (**4a**): Anal. Calcd for $C_{24}H_{24}N_{10}O_2Mn$ (%): C, 53.43; H, 4.45; N, 25.97. Found: C, 53.38; H, 4.52; N, 25.88. [Mn(MeaaiEt)$_2$(NCO)$_2$] (**4b**): Anal. Calcd for $C_{26}H_{28}N_{10}O_2Mn$ (%): C, 55.03; H, 4.93; N, 24.69. Found: C, 55.09; H, 4.85; N, 24.77.

2.4. *[Zn(HaaiMe)$_2$(NCO)$_2$] (6a)*

A methanol solution (15 cm^3) of 1-methyl-2-(pheylazo)imidazole (HaaiEt, 0.32 g, 1.6 mmol) was added dropwise to $Zn(OAc)_2 \cdot 4H_2O$ (0.2 g, 0.78 mmol) in the same solvent (20 cm^3) at room temperature (298 K). An aqueous methanol solution of NaNCO (0.11 g, 1.7 mmol) was then added dropwise. The mixture was stirred for 15 min and filtered, and the filtrate kept undisturbed for a few days. Orange-red crystals were filtered off, washed with cold water and methanol, and dried *in vacuo*. Yield: 0.25 g (58%). All other zinc complexes were prepared by the same procedure and yields were 60–70%. [Zn(HaaiMe)$_2$(NCO)$_2$](**5a**): Anal. Calcd for $C_{22}H_{20}N_{10}O_2Zn$ (%): C, 50.63; H, 3.83; N, 26.85. Found: C, 50.54; H, 3.74; N, 26.80. [Zn(MeaaiMe)$_2$(NCO)$_2$](**5b**): Anal. Calcd for $C_{24}H_{24}N_{10}O_2Zn$ (%): C, 52.42; H, 4.36; N, 25.48. Found: C, 52.33; H, 4.30; N, 25.40. [Zn(HaaiEt)$_2$(NCO)$_2$](**6a**): Anal. Calcd for $C_{24}H_{24}N_{10}O_2Zn$ (%): C, 52.42; H, 4.36; N, 25.48. Found: C, 52.49; H, 4.30; N, 25.40. [Zn(MeaaiEt)$_2$(NCO)$_2$] (**6b**) Anal. Calcd for $C_{26}H_{28}N_{10}O_2Zn$ (%): C, 54.03; H, 4.84; N, 24.24. Found: C, 54.09; H, 4.80; N, 24.19.

2.5. *X-ray structures of [Mn(MeaaiEt)$_2$(NCO)$_2$](4b) and [Zn(HaaiMe)$_2$(NCO)$_2$](5a)*

A summary of crystallographic data and structure refinement parameters is given in table 1. Data were collected with a Siemens SMART CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 294 K for **4b** and at 293 K for **5a**. Unit cell parameters were determined from least-squares refinement of setting angles with 2θ in the range $2.8 \le 2\theta \le 56.6°$ for **4b** and $4.2 \le 2\theta \le 56.6°$ for **5a**. Total data collected were 16773 and 28718 out of which unique data were 6378 and 5838 for **4b** and **5a**, respectively. The *hkl* ranges are $-19 \le h \le 21$, $-11 \le k \le 9$, $-27 \le l \le 27$ for **4b** and $-19 \le h \le 14$, $-22 \le k \le 21$, $-20 \le l \le 24$ for **5a**. Reflection data were recorded using the ω scan technique. Data were corrected for Lp and empirical absorption corrections using the SAINT program. Semi-empirical absorption corrections based on ψ-scans 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. Hydrogen atoms were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual minima and maxima were −0.16, 0.27 for **4b** and −0.29, 0.25 e Å^{-3} for **5a**. All complexes are non-electrolytes.

Table 1. Summary of crystallographic data for [Mn(MeaaiEt)$_2$(NCO)$_2$] (**4b**) and [Zn(HaaiMe)$_2$(NCO)$_2$] (**5a**).

	(**4b**)	(**5a**)
Empirical formula	$C_{26}H_{28}N_{10}O_2Mn$	$C_{22}H_{20}N_{10}O_2Zn$
Formula weight	567.52	521.87
Temperature (K)	294	293
Space group	$P2_1/n$	$Pbca$
Crystal size (mm)	0.30 × 0.20 × 0.20	0.40 × 0.40 × 0.30
Unit cell dimensions		
a (Å)	16.330(2)	14.3525(12)
b (Å)	8.8989(12)	17.3909(14)
c (Å)	20.863(3)	19.2009(15)
β (°)	110.633(3)	
V (Å)^3	2837.4(6)	4792.6(7)
Z	4	8
λ (Å)	0.71073	0.71073
μ (Mo Kα) (mm^{-1})	0.507	1.066
D_{calc} (Mg m^{-3})	1.329	1.446
Refined parameters	352	386
Total collected data	16773	28718
Unique data [$I > 2\sigma(I)$]	6378	5838
R_1^a [$I > 2\sigma(I)$]	0.0391	0.0444
wR_2^b	0.0763	0.1107
Goodness of fit	0.92	0.98

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$.
[b] $wR = [\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0300P)^2]$ for **4b** and $w = 1/[\sigma^2(F_o^2) + (0.0552P)^2]$ for **5a** where $P = (F_o^2 + 2F_c^2)/3$.

3. Result and discussion

3.1. *IR and electronic spectra*

Infrared spectra show very strong bands at 2190–2208 cm^{-1} for both types of complex (**3**–**6**), corresponding to ν(NC) of bound NCO (table 2). Moderately intense stretches at 1585–1600 and 1440–1448 cm^{-1} are due to ν(C=N) and ν(N=N), respectively. Solution electronic spectra of complexes **3** and **4** show intense peaks below 400 nm assigned to ligand centred transitions. Two weak ($\varepsilon \sim 10^3$ M^{-1} cm^{-1}) transitions observed above 440 nm are due to a combination of MLCT and d–d transitions (table 2). The spectroscopic profile supports tetrahedral stereochemistry [15].

3.2. *Molecular structures*

Figures 1 and 2 show the molecular structures of [Mn(MeaaiEt)$_2$(NCO)$_2$] (**4b**) and [Zn(HaaiMe)$_2$(NCO)$_2$] (**5a**), respectively along with the atom numbering schemes used. Selected bond distances and angles are listed in table 3. The neutral complexes consist of a central metal atom surrounded by two ligands and two NCO group. Metal ions sit at the centre of a tetrahedron. All ligands act as monodentates and the imidazole derivatives bond through imidazole–N. The coordination spheres are compressed along the c axis in such a way that three of the N–M–N angles are greater than the tetrahedral angle with values of N(1)–M–N(2), 112.13(8) (Mn), 112.61(12) (Zn); N(1)–M–N(3), 124.64(7) (Mn), 105.36(9) (Zn) and N(2)–Mn–N(3), 115.72(7) and N(2)–Zn(1)–N(7), 117.47(10), N(1)–Zn(1)–N(7), 119.73(9)°. Remaining N–Mn–N angles are less than the tetrahedral angle with values N(1)–Mn–N(7), 102.85(7);

Table 2. Electronic absorption[a], IR[b], and magnetic moment (μ) data.

	Electronic spectrum		IR spectrum (cm^{-1})			
Compound	(λ_{max}/nm)	($10^{-3}\,\varepsilon\,M^{-1}\,cm^{-1}$)	ν(NCO)	ν(C=N)	ν(N=N)	μ (BM)
[Mn(HaaiMe)$_2$(NCO)$_2$] (**3a**)	465(1.96), 382(28.82)	452(3.02), 358(34.98)	2195	1598	1448	6.0
[Mn(MeaaiMe)$_2$(NCO)$_2$] (**3b**)	468(1.65), 384(27.96)	456(2.91), 362(32.15)	2193	1596	1446	5.98
[Mn(HaaiEt)$_2$(NCO)$_2$] (**4a**)	462(1.57), 380(27.81)	454(2.70), 358(33.83)	2196	1597	1447	6.01
[Mn(MeaaiEt)$_2$(NCO)$_2$] (**4b**)	476(1.76), 380(30.17)	444(3.87), 364(32.75)	2194	1598	1448	6.06
[Zn(HaaiMe)$_2$(NCO)$_2$] (**5a**)	438(6.91), 362(46.89)	378(44.40)	2208	1585	1444	
[Zn(MeaaiMe)$_2$(NCO)$_2$] (**5b**)	442(11.69), 372(36.83)	384(37.74)	2198	1597	1439	
[Zn(HaaiEt)$_2$(NCO)$_2$] (**6a**)	438(8.79), 362(48.70)	376(47.35)	2196	1582	1445	
[Zn(MeaaiEt)$_2$(NCO)$_2$] (**6b**)	442(7.03), 370(29.41)	382(28.97)	2208	1599	1448	

[a] In CH_3CN.

[b] In KBr disc.

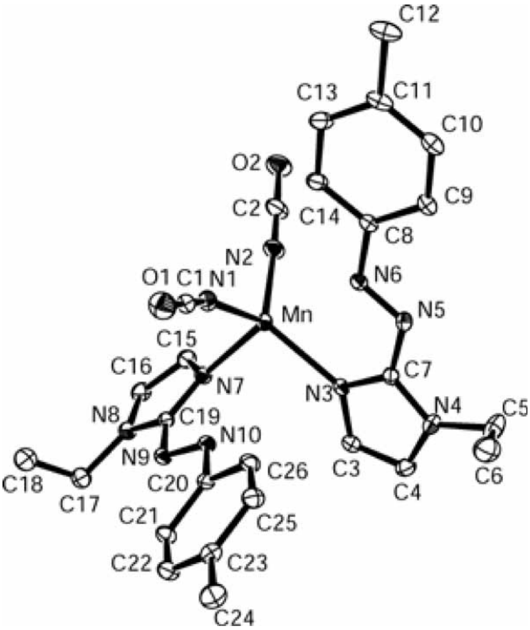


Figure 1. ORTEP figure of [Mn(MeaaiEt)$_2$(NCO)$_2$] (**4b**) showing the atom labelling scheme.

N(2)–Mn–N(7), 96.79(7), N(3)–Mn–N(7), 97.59(6) and N(2)–Zn(1)–N(3), 97.24(11); N(3)–Zn(1)–N(7), 99.42(8)° (table 3). There are two different Mn–N(imidazole) bond lengths: Mn–N(3), 2.1765(15) and Mn-N(7), 2.2145(17) Å. Zn-N(imidazole) distances are shorter than Mn–N(imidazole) distances (Zn(1)–N(3), 2.124(2); Zn(1)–N(7), 2.015(2) Å). Mn–N(NCO) bond distances are slightly shorter than Mn–N(imidazole)

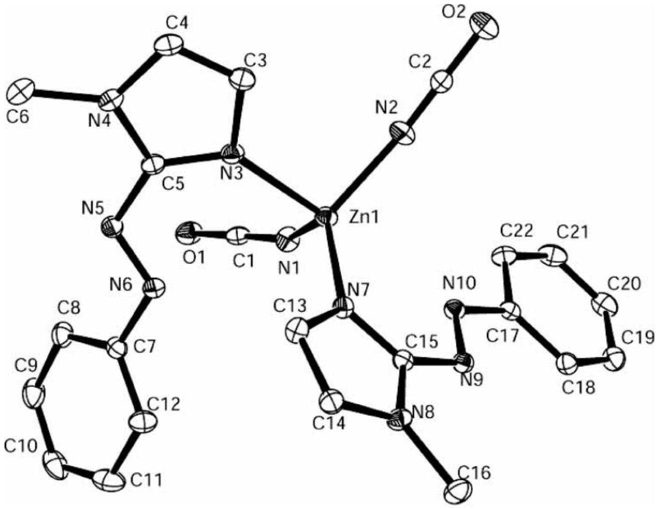


Figure 2. ORTEP figure of [Zn(HaaiMe)$_2$(NCO)$_2$] (**5a**) showing the atom labelling scheme.

Table 3. Selected bond distances and bond angles for **4b** and **5a**.

4b	Bond distances (Å)	**5a**	Bond distances (Å)
Mn–N(1)	2.050(4)	Zn(1)–N(1)	1.944(2)
Mn–N(2)	2.059(3)	Zn(1)–N(2)	1.937(3)
Mn–N(3)	2.174(2)	Zn(1)–N(3)	2.124(2)
Mn–N(7)	2.213(2)	Zn(1)–N(7)	2.0151(19)
N(5)–N(6)	1.261(3)	N(5)–N(6)	1.262(3)
N(9)–N(10)	1.267(3)	N(9)–N(10)	1.263(3)
N(1)–C(1)	1.153(5)	N(1)–C(1)	1.130(4)
N(2)–C(2)	1.140(4)	N(2)–C(2)	1.116(4)
O(1)–C(1)	1.198(5)	O(1)–C(1)	1.201(4)
O(2)–C(2)	1.199(5)	O(2)–C(2)	1.185(4)
N(7)–C(15)	1.353(4)	N(7)–C(15)	1.326(3)
4b	Bond angles (°)	**5a**	Bond angles (°)
N(1)–Mn–N(2)	112.24(13)	N(1)–Zn(1)–N(2)	112.68(12)
N(1)–Mn–N(3)	124.67(11)	N(1)–Zn(1)–N(3)	105.36(10)
N(1)–Mn–N(7)	102.82(10)	N(1)–Zn(1)–N(7)	119.73(9)
N(2)–Mn–N(3)	115.68(11)	N(2)–Zn(1)–N(3)	97.24(10)
N(2)–Mn–N(7)	96.72(10)	N(2)–Zn(1)–N(7)	117.46(10)
N(3)–Mn–N(7)	97.53(9)	N(3)–Zn(1)–N(7)	99.42(8)
Mn–N(1)–C(1)	157.7(3)	Zn(1)–N(1)–C(1)	143.4(2)
Mn–N(2)–C(2)	175.2(4)	Zn(1)–N(2)–C(2)	165.1(3)
O(1)–C(1)–N(1)	178.9(3)	O(1)–C(1)–N(1)	177.1(3)
O(2)–C(2)–N(2)	178.8(3)	O(2)–C(2)–N(2)	179.8(3)

distances. The greater s-character of N in NCO compared to N in imidazole reduces the M–N(CO) distances. N=N bond distances (1.262–1.268 Å) are slightly longer than in the free ligand value (1.258(3) Å) [17]. Structural distortion arising from interactions between the azophenyl groups of the coordinated ligands are manifested by Mn–N and N=N elongation. C(imidazole)–N(azo) lengths are shorter than N(azo)–C(phenyl) distances in the coordinated ligands. All other bond parameters lie within the limits of estimated standard deviations of values for the free ligands [17].

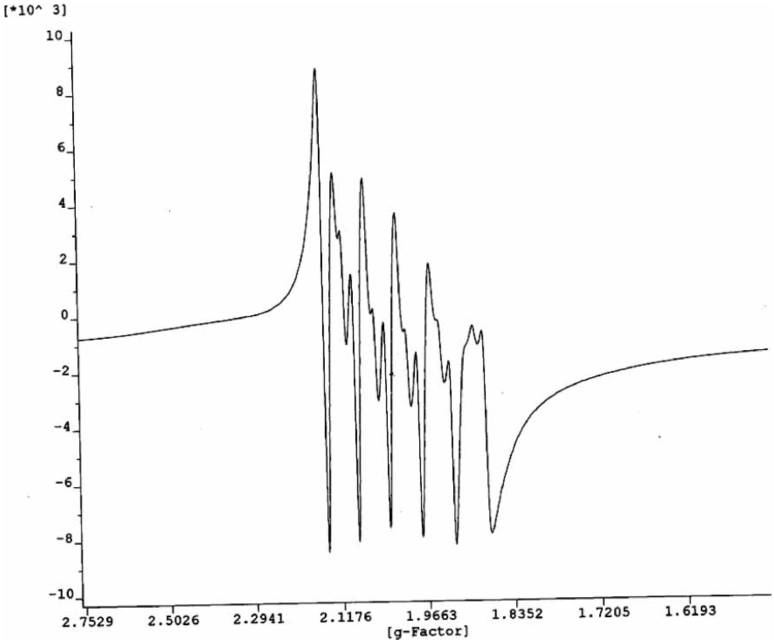


Figure 3. EPR spectrum of [Mn(MeaaiMe)$_2$(NCO)$_2$] (**3b**) at 77 K.

3.3. *EPR spectra and magnetism*

EPR spectra of solutions in MeCN at 77 K display $g \approx 2$, with six hyperfine lines as expected for a ^{55}Mn(II) complex ($I = 5/2$) (figure 3). The hyperfine coupling constant A is 95–100 G. Each hyperfine line shows three split lines at 77 K and the super-hyperfine coupling constant $A_{\perp} = 16$ G. This suggests interaction of ligand–N with Mn(II) · Mn(RaaiR′)$_2$(NCO)$_2$ has a μ_{eff} value of around 6.0 BM at 300 K (table 2), as expected for an isolated $S = 5/2$ Mn(II) monomer.

3.4. *Cyclic voltammetry*

A representative cyclic voltammogram of Mn(HaaiEt)$_2$(NCO)$_2$ (**4a**) is shown in figure 4 and data are summarized in table 4. An irreversible anodic peak (Ep$_a$) is observed at ≥0.95 V *versus* SCE. Two reductive responses are observed negative to SCE and *quasi*-reversibility of the couples is reflected by peak-to-peak separations, $\Delta Ep \geq 100$ mV. Cyclic voltammograms of free ligand and Zinc(II) complexes do not exhibit any oxidative response positive to SCE. $Ep_a \geq 0.95$ V in Mn(RaaiR′)$_2$(NCO)$_2$ is assigned to the Mn(II)/Mn(II) redox process. Redox couples negative to SCE are referred to accommodation of an electron in the LUMO and are assigned to [–N=N–]/[–N=N–]$^-$ and [–N=N–]$^-$/[–N=N–]$^{2-}$, respectively. The first two reductions, −0.5 to −0.7 and −0.7 to −0.9 V, refer to the [–N=N–]/[–N=N–]$^-$ couple of two coordinated ligands in the complex and the more negative, irreversible response (< −1.1 V) may refer to the [–N=N–]/[–N–N–]$^-$ couple. The coordinated ligand has a less negative reduction potential than the free ligand data and potentials follow

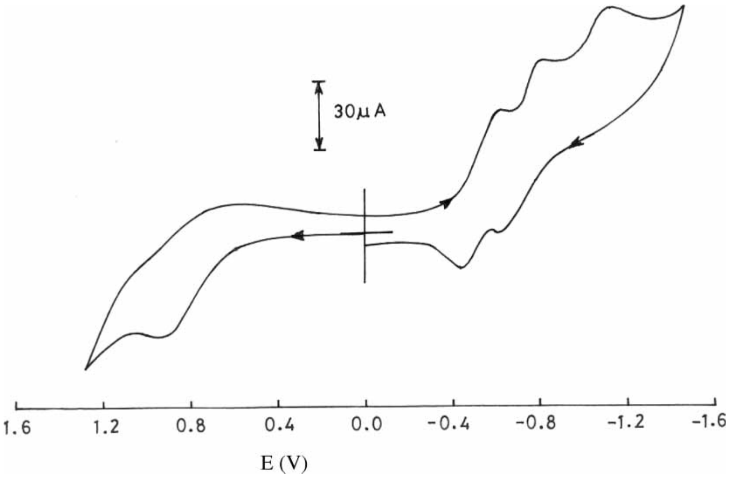


Figure 4. Cyclic voltammogram of $Mn(HaaiEt)_2(NCO)_2$.

Table 4. Cyclic voltammetry[a] data.

Compound	*E*, *V*(ΔEp, mV) for metal oxidation[b]	Ligand reduction		
$[Mn(HaaiMe)_2(NCO)_2]$ **(3a)**	0.95	−0.52 (130)	−0.74 (130)	−1.11[c]
$[Mn(MeaaiMe)_2(NCO)_2]$ **(3b)**	0.92	−0.56 (140)	−0.76 (150)	−1.20[c]
$[Mn(HaaiEt)_2(NCO)_2]$ **(4a)**	0.97	−0.53 (120)	−0.70 (140)	−1.15[c]
$[Mn(MeaaiEt)_2(NCO)_2]$ **(4b)**	0.99	−0.57 (130)	−0.74 (140)	−1.20[c]
$[Zn(HaaiMe)_2(NCO)_2]$ **(5a)**		−0.65 (120)	−0.81 (140)	−1.25[c]
$[Zn(MeaaiMe)_2(NCO)_2]$ **(5b)**		−0.68 (130)	−0.84 (140)	−1.30[c]
$[Zn(HaaiEt)_2(NCO)_2]$ **(6a)**		−0.70 (120)	−0.88 (160)	−1.30[c]
$[Zn(MeaaiEt)_2(NCO)_2]$ **(6b)**		−0.73 (120)	−0.90 (150)	−1.35[c]

[a] Solvent MeCN, Pt-disk with working electrode, SCE, Pt-wire, $[nBu_4N][ClO_4]$, $E = 0.5(Ep_a + Ep_c)$, $\Delta Ep = |Ep_a - Ep_c|$, Ep_a = anodic peak potential, Ep_c = cathodic peak potential.
[b] Ep_a.

the order $RaaiR' \ll Zn(RaaiR')_2(NCO)_2 < Mn(RaaiR')_2(NCO)_2$. This indicates that Mn(II) is a better acceptor than Zn(II) in these complexes.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 258584 for $[Mn(MeaaiEt)_2(NCO)_2]$ (**4b**) and CCDC 258585 for $[Zn(HaaiMe)_2(NCO)_2]$ (**5a**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1FZ, UK.

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References

[1] T.K. Misra, D. Das, C. Sinha, P. Ghosh, C.K. Pal. *Inorg. Chem.*, **37**, 1672 (1998).
[2] P. Byabartta, Sk. Jasimuddin, B.K. Ghosh, C. Sinha, A.M.Z. Slawin, J.D. Woollins. *New J. Chem.*, **26**, 1415 (2002).
[3] P. Byabartta, J. Dinda, P.K. Santra, C. Sinha, K. Paneerselvam, F.-L. Liao, T.-H. Lu. *J. Chem. Soc., Dalton Trans.*, 2825 (2001).
[4] J. Dinda, D. Das, P.K. Santra, C. Sinha, L.R. Falvello. *J. Organomet. Chem.*, **629**, 28 (2001).
[5] S. Pal, D. Das, C. Sinha, C.H.L. Kennard. *Inorg. Chim. Acta*, **313**, 21 (2001).
[6] U.S. Ray, Sk. Jasimuddin, B.K. Ghosh, M. Monfort, J. Ribas, G. Mostafa, T.-H. Lu, C. Sinha. *Eur. J. Inorg. Chem.*, 250 (2004).
[7] U.S. Ray, D. Banerjee, C. Sinha. *Proc. Indian Acad Sci. (Chem. Sci.)*, **115**, 169 (2003).
[8] U.S. Ray, B.G. Chand, G. Mostafa, J. Cheng, T.-H. Lu, C. Sinha. *Polyhedron*, **22**, 2587 (2003).
[9] U.S. Ray, D. Banerjee, J.-C. Liou, C.-N. Lin, T.-H. Lu, C. Sinha. *Inorg. Chim. Acta* (In press).
[10] U.S. Ray, D. Banerjee, G. Mostafa, T.-H. Lu, C. Sinha. *New J. Chem.*, **28**, 1437 (2004).
[11] J. Dinda, Sk. Jasimuddin, G. Mostafa, C.-H. Hung, C. Sinha. *Polyhedron*, **23**, 793 (2004).
[12] B.G. Chand, U.S. Ray, J. Cheng, T.-H. Lu, C. Sinha. *Polyhedron*, **22**, 1213 (2003).
[13] B.G. Chand, G. Mostafa, T.-H. Lu, L.R. Falvello, C. Sinha. *Polyhedron*, **22**, 3161 (2003).
[14] B.G. Chand, U.S. Ray, P.K. Santra, G. Mostafa, T.-H. Lu, C. Sinha. *Polyhedron*, **22**, 1205 (2003).
[15] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, Elsevier Science, Amsterdam (1984).
[16] H. Eklund, C.I. Branden. In *Zinc Enzymes*, T.G. Spiro (Ed.), p. 124, Wiley, New York (1983).
[17] D. Das. Ph.D Thesis, Burdwan University, Burdwan, India (1998).