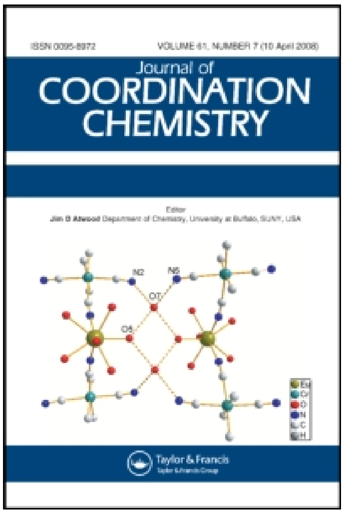

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Tetrahedral manganese(II) complexes of 1-alkyl-2-(arylazo)imidazoles. X-ray crystal structure of $[Mn(HaaiMe)_4](ClO_4)_2 \cdot DMF$ (HaaiMe = 1-methyl-2-(phenylazo)imidazole)

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Tetrahedral manganese(II) complexes of 1-alkyl-2-(arylazo)imidazoles. X-ray crystal structure of $[Mn(HaaiMe)_4](ClO_4)_2 \cdot DMF$ (HaaiMe = 1-methyl-2-(phenylazo)imidazole)

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$[Mn(RaaiR')_4](ClO_4)_2$ complexes have been synthesised by reacting $Mn(ClO_4)_2 \cdot 6H_2O$ and RaaiR′ in methanol (RaaiR′ = 1-alkyl-2-arylazo)imidazole, R = H (**a**), Me (**b**), Cl (**c**); R′ = Me (**1**), Et (**2**)). The orange–red crystalline compounds were characterised by microanalytical, spectroscopic, magnetic, thermal and electrochemical data. A single-crystal X-ray diffraction study of a DMF adduct of **1a** revealed tetrahedral orientation of four ligands coordinating through imidazole-*N* while the azophenyl group (–N=N–Ph) is pendant. Cyclic voltammetry shows the Mn(III)/Mn(II) couple at > 1.0 V along with azo reductions.

Keywords: Arylazoimidazoles; Manganese(II); Tetrahedral; X-ray structure

1. Introduction

Manganese plays an essential structural or catalytic role in many proteins. The active Mn sites of many enzymes have been shown to bind with imidazole nitrogen from histidine residues [1–4]. It is therefore of interest to synthesize ligands containing imidazole groups and their manganese complexes. There are different strategies for the incorporation of an imidazolyl moiety into a ligand [5–7]. We have adopted the simple technique of diazotisation to anchor $Ar–N{=}N^+$ to the imidazole backbone to yield 2-(arylazo)imidazoles [8–19]. Imidazole bears two *N*-donor centers, N(1) and N(3), of different hardness. Thus, imidazole can selectively bind metal ions: N(1) prefers to bind soft metal ions and N(3) coordinates with hard cations [19]. N(1)-alkylation eliminates the bridging ability of imidazole [3] and we have synthesized several

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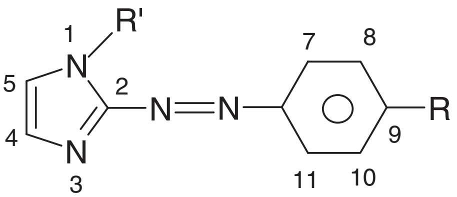
1-alkyl-2-(arylazo)imidazoles (RaaiR′). A structural investigation so far reported concerning metal complexes of RaaiR′ has revealed that the platinum metals Ru(II) [8,9], Os(II) [10], Pd(II) [11] and Pt(II) [12] form derivatives in which the ligand behaves as a bidentate imidazole-*N*, azo-*N* chelate, while in complexes of 3d-transition metals [13–15] and nontransition Group 12 elements [16–18] (Zn(II), Cd(II) Hg(II)) RaaiR′ binds either as a monodentate (imidazole-*N*) or a bidentate chelate.

Manganese(II)-azido complexes of RaaiR′ have been reported in which N_3^- acts as EO and EE bridges to form a 1D chain and which exhibit interesting local ferromagnetic and global antiferromagnetic coupling. The spin canting phenomenon is responsible for the distorted octahedral geometry which is manifested by an unusually long Mn–N(azo) distance [15]. This has encouraged us to synthesize other different types of Mn(II) complexes. In this work we report Mn(II) complexes of RaaiR′ using $Mn(ClO_4)_2 \cdot H_2O$ as a reagent.



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

2. Experimental

2.1. *Materials*

Published methods [8] were used to prepare 1-alkyl-2-(arylazo)imidazoles [RaaiR′ where R = H (**a**), Me (**b**), Cl (**c**); R′ = Me (**1**), Et (**2**)]. $Mn(ClO_4)_2 \cdot 6H_2O$ was prepared by adding $MnCO_3$ to warm $HClO_4$ solution (1 : 1, v/v) and recrystallisation from water in the presence of a few drops of $HClO_4$. All other chemicals and organic solvents used were of reagent grade as received from SRL, India. Purification of MeCN and preparation of $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{ClO}_4]$ were carried out following literature methods [10].

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, reflectance spectra, Jasco UV-VIS/NIR model V-570; IR spectra (KBr disk, 4000–200 cm^{-1}), Jasco FT-IR model 420. Conductances were measured using a Systronics 304 model conductivity meter (solute concentration $\sim 10^{-3}$ M) in MeCN. Estimation of manganese was carried out by microwave digestion followed by potassium periodate oxidation to pink permanganate [20]. Electrochemistry was carried out using PAR electrochemistry system; 250 potentiostat/versastat and 270 software package. In cyclic voltammetry the following conditions were used: solvent, dry MeCN; supporting electrolyte, [nBu$_4$N][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. All experiments were done under a dry N_2 atmosphere at 295(2) K. ESR spectra were measured in MeCN solution at room temperature (298 K) and liquid nitrogen temperature (77 K) using a Bruker ESR spectrometer, model EMX 10/12 with an X-band ER 4119 HS cylindrical resonator.

2.3. *Tetrakis(1-methyl-2-(phenylazo)imidazole)manganese(II) percholate monohydrate, [Mn(HaaiMe)$_4$](ClO$_4$)$_2\cdot$H$_2$O (1a)*

A methanolic solution (15 cm^3) of 1-methyl-2-(phenylazo)imidazole (HaaiMe, 0.3 g, 1.61 mmol) was added dropwise to Mn(ClO$_4$)$_2\cdot$6H$_2$O (0.2 g, 0.56 mmol) in the same solvent (20 cm^3) at room temperature (298 K). The mixture was stirred for 15 min and a small amount of yellow material was filtered off, and the filtrate was kept undisturbed for a few days. Bright, orange–red crystalline product was filtered off and washed with cold water and methanol. Finally it was dried *in vacuo*. Isolated yield was 0.25 g (61%).

All other complexes were prepared by the same procedure and yields varied from 60–70%. Data for the complexes are as follows: [Mn(HaaiMe)$_4$](ClO$_4$)$_2\cdot$H$_2$O (**1a**): *Anal.* Found: C, 47.14; H, 4.02; N, 22.15; Mn, 5.60. Calc. for $C_{40}H_{42}N_{16}O_9Cl_2Mn$: C, 47.25; H, 4.13; N, 22.05; Mn, 5.41%. IR (KBr disk) (cm^{-1}); ν(H$_2$O), 3416(b); ν(ClO$_4$), 1089(s), 626(w); ν(C=N), 1584(m); ν(N=N), 1438(m). [Mn(MeaaiMe)$_4$](ClO$_4$)$_2\cdot$H$_2$O (**1b**): *Anal.* Found: C, 49.18; H, 4.74; N, 21.02; Mn, 5.30. Calc. for $C_{44}H_{50}N_{16}O_9Cl_2$ Mn: C, 49.26; H, 4.66; N, 20.90; Mn, 5.13%. IR (KBr disk) (cm^{-1}); ν(H$_2$O), 3414(b); ν(ClO$_4$), 1093(s), 624(w); ν(C=N), 1583(m); ν(N=N), 1444(m). [Mn(ClaaiMe)$_4$] (ClO$_4$)$_2\cdot$H$_2$O (**1c**): *Anal.* Found: C, 41.71; H, 3.20; N, 19.54; Mn, 4.91. Calc. for $C_{40}H_{38}N_{16}Cl_6O_8Mn$: C, 41.60; H, 3.29; N, 19.41; Mn, 4.76%. IR (KBr disk) (cm^{-1}); ν(H$_2$O), 3416(b); ν(ClO$_4$), 1089(s), 627(w); ν(C=N), 1591(m); ν(N=N), 1446(m). [Mn(HaaiEt)$_4$](ClO$_4$)$_2\cdot$H$_2$O (**2a**): *Anal.* Found: C, 49.34; H, 4.60; N, 21.05; Mn, 5.31. Calc. for $C_{44}H_{50}N_{16}O_9Cl_2Mn$: C, 49.26; H, 4.66; N, 20.90; Mn, 5.13%. IR (KBr disk) (cm^{-1}); ν(H$_2$O), 3416(b); ν(ClO$_4$), 1089(s), 626(w); ν(C=N), 1585(m); ν(N=N), 1436(m). [Mn(MeaaiEt)$_4$] (ClO$_4$)$_2\cdot$H$_2$O (**2b**): *Anal.* Found: C, 51.00; H, 5.08; N, 20.00; Mn, 4.92. Calc. for $C_{48}H_{58}N_{16}O_9Cl_2Mn$: C, 51.07; H, 5.14; N, 19.86; Mn, 4.87%. IR (KBr disk) (cm^{-1}); ν(H$_2$O), 3416(b); ν(ClO$_4$), 1091(s), 626(w); ν(C=N), 1595(m); ν(N=N), 1448(m). [Mn(ClaaiEt)$_4$](ClO$_4$)$_2\cdot$H$_2$O (**2c**): *Anal.* Found: C, 43.52; H, 3.88; N, 18.62; Mn, 4.68. Calc. for $C_{44}H_{46}N_{16}O_9Cl_6Mn$: C, 43.64; H, 3.80; N, 18.51; Mn, 4.54%. IR (KBr disk) (cm^{-1}); ν(H$_2$O), 3416(b); ν(ClO$_4$), 1089(s), 626(w); ν(C=N), 1584(m); ν(N=N), 1438(m).

2.4. *Ion exchange*

2.4.1. Transmetallation. To a CH$_2$Cl$_2$–MeOH (1:1, v/v) (20 cm^3) solution of [Mn(MeaaiMe)$_4$](ClO$_4$)$_2$ (0.15 g, 0.14 mmol), Cd(ClO$_4$)$_2\cdot$6H$_2$O (0.07 g, 0.17 mmol) in MeOH was added with stirring for 1 h. The solution colour changed from orange to orange–yellow. The solution was left overnight to evaporate in the air.

Orange material that was formed was filtered off and washed with water and cold methanol. The complex was recrystallized from CH_2Cl_2–MeOH (1 : 1, v/v). Infrared, electronic spectra and magnetic moment data were comparable to data for [Cd(MeaaiMe)$_4$] $(ClO_4)_2$ [18]. Yield: 0.11 g, 71%.

2.4.2. Anion exchange. To an aqueous suspension of [Mn(MeaaiMe)$_4$]$(ClO_4)_2$ (0.15 g, 0.14 mmol), KI (0.12 g, 0.72 mmol) solution was added and the mixture stirred for 5 days. The resulting orange suspension was filtered off, washed with water and dried over $CaCl_2$. Infrared spectra showed the absence of $\nu(ClO_4)$ and supports anion exchange. The same reaction was carried out with NH_4PF_6 or $K_3[Fe(CN)_6]/K_4[Fe(CN)_6)]$ and infrared spectra also support anion exchange. However, we could not optimize time or conditions for anion exchange. Incomplete anion exchange during early stages of reaction was evident by observations of $\nu(ClO_4)$, $\nu(PF_6)$ and $\nu(CN)$.

2.5. *X-ray structure of [Mn(HaaiMe)$_4$](ClO$_4$)$_2$ · DMF*

Crystals obtained from methanol solution did not diffract, perhaps because of rapid loss of water of crystallization. X-ray-quality crystals of a DMF adduct were grown by adding few drops of DMF to a methanolic solution of the original salt. Data for the adduct were collected on a Siemens SMART CCD diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Unit cell parameters were determined from least-squares refinement of setting angles with 2θ in the range $4.28 \le 2\theta \le 49.96°$. Total data collected were 8810 out of which unique data were 8605. The *hkl* ranges are $0 \le h \le 30$, $0 \le k \le 18$, $-29 \le l \le 29$.

Table 1. Crystallographic data for [Mn(HaaiMe)$_4$]$(ClO_4)_2$ · DMF.

	[Mn(HaaiMe)$_4$]$(ClO_4)_2$. DMF (4a)
Empirical formula	$C_{40}H_{40}N_{16}O_8Cl_2$ Mn · $0.5C_3H_7NO$
Formula weight	1035.27
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	*C*2/*c*
Crystal size (mm)^3	0.30 × 0.30 × 0.20
Unit cell dimensions	
a (Å)	25.83(2)
b (Å)	15.324(10)
c (Å)	25.001(??)
β (°)	97.10(4)
V (Å)^3	9821(11)
Z	8
λ (Å)	0.71073
μ(Mo Kα) (mm^{-1})	0.446
D_{calc} (mg m^{-3})	1.400
Refined parameters	666
Observed data [$I > 2\sigma(I)$]	8605
R_1[a][$I > 2\sigma(I)$]	0.0594
wR_2[b]	0.1395
Goodness of fit	0.93

[a] $R = \Sigma|F_0 - F_c|/\Sigma F_0$. [b] $wR_2 = [\Sigma w(F_0{}^2 - F_c{}^2)]/\Sigma[w(F_0{}^4]^{1/2}]^2$, $w = 1/[\sigma^2(F_0{}^2) + (0.00P)^2]$ where $P = (F_0^2 + 2\ F_c^2)/3$.

A summary of crystallographic data and structure refinement parameters is given in table 1. Reflection data were recorded using the ω scan technique and were corrected for Lorentz polarization effects and linear decay. 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. The hydrogen atoms were fixed geometrically and refined using the riding model. In the final difference Fourier map the residual minima and maxima were -0.693 and $0.663\,\mathrm{e\,\AA^{-3}}$.

3. Results and discussion

3.1. *Synthesis and formulation*

1-Alkyl-2-(arylazo)imidazoles (RaaiR′) (**1, 2**) belong to the azoimine (–N=N–C=N–) family of ligands. They may serve either as monodentate imidazole-*N* donors or bidentate imidazole-*N*(*N*), azo-*N*(*N*′) chelates [8–18]. Ligands reacted in methanol with $Mn(ClO_4)_2 \cdot 6H_2O$ at a 3:1 stoichiometry (ligand:metal) did not give $[Mn(N,N')_3](ClO_4)_2$. The compositions of the complexes have been determined by microanalysis (C, H, N, Mn) and spectroscopic studies. Molar conductance measurements indicate the existence of 1 : 2 electrolytes in MeCN ($\lambda_M = 170–200\ ^{-1}\Omega^{-1}\,cm^2\,mol^{-1}$). The complexes isolated are tetrakis tetrahedral $[Mn(RaaiR')_4](ClO_4)_2 \cdot H_2O$. A single crystal X-ray structure of a DMF adduct of **1a** confirms the geometry.

3.2. *Spectral and magnetic studies*

Infrared spectra show a very strong, unstructured band centered at 1090 cm^{-1} with a weak stretch at 625 cm^{-1} due to $\nu(ClO_4)$. Moderately intense stretches at 1580–1590 and 1420–1430 cm^{-1} are due to ν(C=N) and ν(N=N), respectively. Lattice water shows a broad, medium intensity band centred at 3410 cm^{-1}. Solution electronic spectra of the complexes show intense absorption at < 400 nm assigned to ligand centred transitions. Two weak ($\varepsilon \sim 10^3\,dm^3\,mol^{-1}\,cm^{-1}$) transitions are observed at > 440 nm and may be referred to a combination of MLCT and d–d transitions (table 2). The spectroscopic profile supports tetrahedral Mn(II) stereochemistry [21].

The magnetic moments, μ_{eff}, are around 6.0 BM at 300 K (table 2), as expected for an isolated $S = 5/2$ Mn(II) monomer. EPR spectra of solutions in MeCN at 77 K display a $g \approx 2$, $m_s = +1/2$ to $-1/2$ fine structure transition split into six hyperfine lines as expected for a ^{55}Mn(II) complex ($I = 5/2$) along with superfine splitting. A notable feature of the spectra is the relatively low value of the hyperfine coupling constant, A, 85–90 G. Each hyperfine line shows splitting at 77 K, suggesting interaction of ligand–N with Mn(II). Low hyperfine coupling constants (A) and high spin magnetic moment data are secondary evidence for tetrahedral Mn(II) stereochemistry [22].

3.3. *Molecular structure of $[Mn(HaaiMe)_4](ClO_4)_2 \cdot DMF$*

Figure 1 shows the molecular structure of the complex $[Mn(HaaiMe)_4](ClO_4)_2 \cdot DMF$ along with the atom numbering scheme used. Selected bond distances and angles are listed in table 3. The cationic complex consists of a central manganese atom surrounded by four HaaiMe ligands. Mn sits at the centre of a tetrahedron. HaaiMe acts as a monodentate ligand and binds through imidazole-*N*. The coordination environment

Table 2. Selected bond distances and bond angles for the DMF adduct.

Mn(1)–N(1)	2.178(3)	N(1)–Mn(1)–N(5)	135.06(11)
Mn(1)–N(5)	2.211(3)	N(1)–Mn(1)–N(9)	99.88(12)
Mn(1)–N(9)	2.194(3)	N(1)–Mn(1)–N(13)	98.94(12)
Mn(1)–N(13)	2.193(3)	N(5)–Mn(1)–N(9)	98.54(12)
N(3)–N(4)	1.254(4)	N(1)–Mn(1)–N(5)	96.91(11)
N(7)–N(8)	1.266(4)	N(5)–Mn(1)–N(13)	96.91(11)
N(11)–N(12)	1.263(4)	N(9)–Mn(1)–N(13)	134.07(12)
N(15)–N(16)	1.268(4)	Mn(1)–N(1)–C(1)	131.7(3)
N(3)–C(3)	1.406(4)	Mn(1)–N(1)–C(3)	122.5(2)
N(4)–C(5)	1.433(4)	Mn(1)–N(5)–C(11)	130.5(3)
N(7)–N(13)	1.391(5)	Mn(1)–N(5)–C(13)	120.4(2)
N(8)–C(15)	1.420(5)	Mn(1)–N(9)–C(21)	128.7(2)
N(11)–C(23)	1.376(5)	Mn(1)–N(9)–C(23)	124.0(3)
N(12)–C(25)	1.404(5)	Mn(1)–N(13)–C(31)	131.4(3)
N(15)–C(33)	1.393(5)	Mn(1)–N(13)–C(33)	106.6(3)
N(16)–C(35)	1.431(5)	O(5)–Cl(2)–O(6)	63.0(16)
Cl(1)–O(1)	1.349(5)	O(6)–Cl(2)–O(8)	129.8(16)
Cl(1)–O(2)	1.368(4)	O(8)–Cl(2)–O(5)	77.0(18)
Cl(1)–O(3)	1.453(8)	O(6)–Cl(2)–O(7)	115.3(6)
Cl(1)–O(4)	1.506(5)	O(5)–Cl(2)–O(7)	107.9(7)
Cl(2)–O(5)	1.361(8)	O(7)–Cl(2)–O(8)	104.6(11)
Cl(2)–O(6)	1.328(10)	O(1)–Cl(1)–O(2)	117.8(4)
Cl(2)–O(7)	1.373(4)	O(1)–Cl(1)–O(3)	117.1(4)
Cl(2)–O(8)	1.369(17)	O(2)–Cl(1)–O(3)	116.4(4)
		O(1)–Cl(1)–O(4)	102.5(3)
		O(2)–Cl(1)–O(4)	101.5(3)
		O(3)–Cl(1)–O(4)	95.8(6)

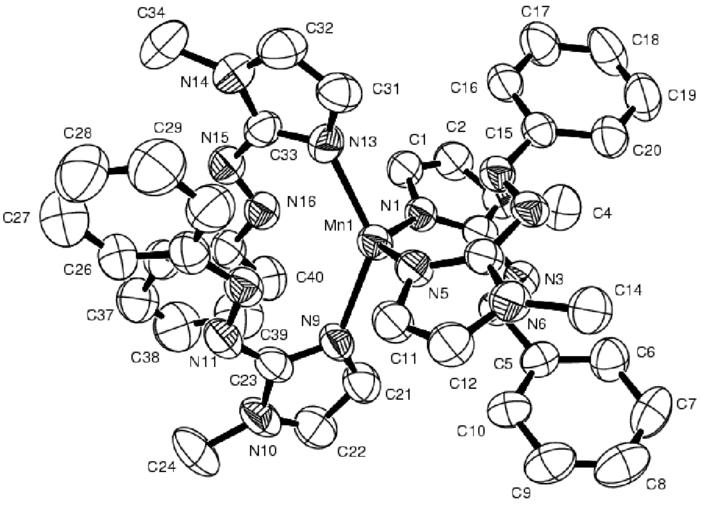


Figure 1. ORTEP view of $[Mn(HaaiMe)_4]^{+2}$ showing the atom labelling scheme.

about Mn is compressed along the crystallographic *c* axis in such a way that two of the N–Mn–N angles are greater than the tetrahedral angle, with values N(1)–Mn(1)–N(5) 135.06(11) and N(9)–Mn(1)–N(13) 134.07(12)°. The remaining N–Mn–N angles are less than 100° (table 2). There are three substantially different Mn–N bond lengths in the range 2.178(3) to 2.211(3) Å; N=N bond distances lie between 1.254(4) to 1.268(4) Å.

Table 3. Electronic spectra[a], cyclic voltammetry[b] and magnetic moment μ data for the complexes.

	Electronic spectra data	Cyclic voltammetry data				
Compound	λ_{max}/nm ($10^{-3}\,\varepsilon$ $M^{-1}\,cm^{-1}$)	Mn^{III}/Mn^{II}	Ligand reduction[c]			μ (BM)
$[Mn(HaaiMe)_4](ClO_4)_2 \cdot H_2O$ (**3a**)	467 (3.20), 445 (3.41), 400 (13.53)	1.21 (100)	−0.30	−0.70	−1.25	6.06
$[Mn(MeaaiMe)_4](ClO_4)_2 \cdot H_2O$ (**3b**)	466 (3.92), 450 (5.25), 400 (14.26)	1.10 (120)	−0.33	−0.75	−1.27	6.12
$[Mn(HaaiEt)_4](ClO_4)_2 \cdot H_2O$ (**4a**)	466 (3.74), 446 (5.21), 400 (13.74)	1.17 (100)	−0.34	−0.78	−1.31	6.11
$[Mn(MeaaiEt)_4](ClO_4)_2 \cdot H_2O$ (**4b**)	464 (4.06), 452 (4.24), 400 (14.39)	1.06 (120)	−0.41	−0.84	−1.35	6.01
$[Mn(ClaaiMe)_4](ClO_4)_2 \cdot H_2O$ (**3c**)	470 (3.08), 453 (4.85), 400 (12.80)	1.28 (120)	−0.26	−0.65	−1.29	6.04
$[Mn(ClaaiEt)_4](ClO_4)_2 \cdot H_2O$ (**4c**)	476 (2.89), 455 (4.36), 400 (13.94)	1.24 (110)	−0.29	−0.70	−1.32	6.08

[a]Solvent: methanol. [b]Solvent: MeCN. [c]Ep_c, V.

The lower limit [1.254(4) Å] is close to the free ligand value [1.258(3) Å] [23]. The structural distortion may arise from steric interactions between the azophenyl groups, as manifested by Mn–N and N=N elongation. The C(imidazole)–N(azo) lengths are shorter than N(azo)–C(phenyl) distances in all four HaaiMe ligands. This is in support of a stronger interaction of azo-*N* with the imidazole ring compared with the phenyl group. All other bond parameters are normal with respect to the free ligands [23]. Each molecular unit carries a half of a molecule of DMF solvent of crystallization. Imidazole, azo and phenyl groups are coplanar and the pendant azophenyl group is oriented in such a way as to reduce steric and electronic repulsion. Two ClO_4^- anions balance the charge of the complex and they do not show any significant interactions with the cation.

3.4. *Cyclic voltammetry*

Redox properties of the manganese complexes have been studied by cyclic voltammetry (CV) using a platinum working electrode. Voltammogram data are collected in table 3. A couple at $> 1.0\,V$ *versus* SCE is due to Mn(III)/Mn(II) redox [22]. The *quasi*-reversibility of the process is indicated by the peak-to-peak separation, $\Delta E\mathrm{p} > 100\,\mathrm{mV}$. The one electron nature of the redox process has been confirmed by current height data for $Fe(CN)_6^{3-}/Fe(CN)_6^{-4}$. Ligand reductions are irreversible and $E\mathrm{p_c}$ values are near to free ligand values. The reduction corresponds to electron accommodation in azo-dominated orbitals.

3.5. *Ion-exchange properties*

Bond distance data obtained from X-ray structure determination of arylazoimidazole complexes of transition [8–15] and non-transition [16–18] metals show that Zn(II), Cd(II), Hg(II) and Ag(I) have a strong preference for imidazole-*N* rather than azo-*N*, while transition metals like Ru(II) and Os(II) have a reverse preference. The 3-d block metal ions Fe(II), Co(II), Ni(II), Cu(II) exhibit mixed preferences depending on co-ligands that are present. Addition of $Cd(ClO_4)_2$ to $[Mn(MeaaiMe)_4](ClO_4)_2$ in CH_2Cl_2–MeOH and stirring for 2 h gave $[Cd(MeaaiMe)_4](ClO_4)_2$. Spectroscopic identification and comparison with reported results [18] support the ion exchange phenomenon. This confirms the weak Mn–N(imidazole) bond compared with the Cd–N(imidazole) bond.

Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 247425, for $[Mn\,(HaaiMe)_4](ClO_4)_2 \cdot DMF$. 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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