

Synthesis, spectral characterization and redox properties of iron (II) complexes of 1-alkyl-2-(arylo)imidazole

U S RAY, D BANERJEE and C SINHA*

Department of Chemistry, The University of Burdwan, Burdwan 713 104,
India
e-mail: c_r_sinha@yahoo.com

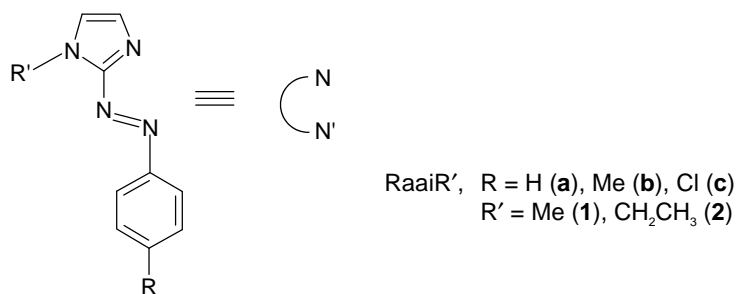
MS received 26 February 2003; revised 12 May 2003

Abstract. Iron (II) complexes of 1-alkyl-2-(arylo)imidazoles (p -R-C₆H₄-N=N-C₃H₂NN-1-R', R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**1/3**), Et (**2/4**) have been synthesized and formulated as *tris*-chelates Fe(RaaiR')₃²⁺. They are characterized by microanalytical, conductance, UV-Vis, IR, magnetic (polycrystalline state) data. The complexes are low spin in character, t_{2g}^6 (Fe(II)) configurations.

Keywords. Aryloimidazole; Fe(II) complexes; *tris*-chelates.

1. Introduction

Aryloheterocycles and their chemistry of transition and non-transition metals have been explored for more than two decades.¹ Owing to their pH-response, photoactivity, light electron communication, stabilization of low valent metal oxidation state, exhibition of serial redox states of complexes, isolation of anion radicals, metal-ion specific solid-phase extracting phenomena, anticancer medicine etc. different groups of researchers^{1–48} have tried to design newer azoheterocycles and their metal complexes and to explore their properties. We have also been engaged for the last few years in trying to enrich this field of chemistry.



We have designed two new classes of arylazoheterocycles: 1-alkyl-2-(arylo)imidazoles^{30–40} and 2-(arylo)pyrimidines.^{41–44} Emphasis is laid on 2-(arylo)imidazoles because of biological importance of imidazole^{49,50} and synthetic simplicity over other azoheterocycles. In continuation of our comprehensive studies on the coordinating

*For correspondence

properties of 1-alkyl-2-(arylo)imidazoles (RaaiR', **1**) R' = Me (**1**), Et (**2**) this paper describes the synthesis, spectroscopic characterization and redox properties of a series of new iron(II) complexes.

2. Experimental

2.1 Materials

All reagents were of analytical grade and were used without further purification. 1-Alkyl-2-(arylo)imidazoles (RaaiR') were synthesized and characterized as per reported procedure.^{30,31} Solvents (MeOH, MeCN for electrochemistry) were purified by known methods.³²⁻³⁴

2.2 Analytical measurements

Microanalytical data (C, H, N) were collected using a Perkin-Elmer 2400 CHN analyser. Iron analysis was carried out by AAS studies.⁵¹ Molar conductance of the complexes were recorded on a direct reading Systronic 304 model conductivity meter using 10^{-3} M solutions. Magnetic susceptibilities were measured by the vibrating sample 155 magnetometer at 298 K. IR and UV-Vis spectra were recorded on Jasco FTIR model 420 and Jasco UV/Vis/NIR model V-570 spectrophotometers. The electrochemistry of the complexes have been examined by cyclic voltammetry with EG and G PARC electrochemistry equipment at Pt-disk working electrode in CH₂Cl₂-MeOH (1:1, *v/v*). Pt-wire auxiliary electrode and potentials are expressed with reference to the potential of SCE. Cyclic voltammograms of the complexes were drawn within the potential range +1.5 to -1.5 V vs SCE.

2.3 Synthesis of complexes

Reaction condition has been set up following previously reported Fe(II)-complexes of 2-(arylo) pyridines.¹ Synthesis of a representative complex is detailed below.

2.3a Iron (II) complexes, [Fe(RaaiR₃)I₂] (3, 4) [Fe(HaaiMe₃)I₂] (3a): An aqueous methanolic solution containing FeSO₄·7H₂O (0.07 g, 0.25 mmol) and HaaiMe (0.14 g, 0.75 mmol) was warmed and to this solution concentrated KI solution was added. The solution was stirred vigorously under N₂ atmosphere for 3 h and cooled in a refrigerator to 5-10°C; green crystals were deposited.

They were collected by filtration, washed with cold water, and MeOH and finally by Et₂O. It was dried *in vacuo* over CaCl₂. Yield, 0.15 g, 68%.

All other complexes were prepared following identical procedure and the yield was varied from 65-70%.

3. Results and discussion

3.1 Synthesis and formulation

The ligands, RaaiR', belong to the unsymmetric N, N'-chelating system. The donor centres N(imidazole) and N(azo) are denoted by N and N' respectively. From an aqueous

solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and RaaiR' in methanol in 1 : 3 mole ratio in presence of excess of KI, we have isolated green coloured crystalline products of composition $[\text{Fe}(\text{RaaiR}')_3]\text{I}_2$ (**3,4**). Addition of saturated solution of $\text{NaClO}_4/\text{NH}_4\text{PF}_6$ also affords complexes of the same composition $[\text{Fe}(\text{RaaiR}')_3][(\text{ClO}_4)_2/(\text{PF}_6)_2]$. The perchlorate salts, $[\text{Fe}(\text{RaaiR}')_3](\text{ClO}_4)_2$ are relatively less stable in solution and slowly change from green to orange yellow compared to PF_6^- and I^- salts. The commercially available PF_6^- -salts, $\text{NH}_4\text{PF}_6/\text{KPF}_6$ are expensive, hence we have examined the properties of complexes with iodide salts, $[\text{Fe}(\text{RaaiR}')_3]\text{I}_2$. Microanalytical data support the composition of the complexes. The molar conductance measurement ($\Lambda_M = 140\text{--}170 \Omega^{-1} \text{cm}^{-1}$) suggests 1 : 2 electrolyte nature of the complexes. The complexes are diamagnetic and support low spin t_{2g}^6 electronic configuration.

3.2 IR spectra

The most plausible assignments of the IR bands useful for establishing the coordination modes of the title complexes have been compared with free ligand values.³⁷ The most significant difference has been observed in the azoimine function. The $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ appear at 1580–1600 and 1380–1390 cm^{-1} in Fe(II)-complexes and are shifted to lower frequency by 20–50 cm^{-1} compared to free ligand values.^{30,31} This is in support of the ρ -acidic character of the azoimine group, while Fe(II) shows ρ -back donation. This is common with complexes of azoimidazoles in higher congeners of group VIII, ruthenium and osmium, of iron.^{32–36} $\nu(\text{Fe}-\text{N})$ may appear at 320–330 cm^{-1} which is absent in the free ligand spectra.

3.3 Absorption spectra

UV-Vis spectral studies of the complexes exhibit transition at lower than 400 nm corresponding to intramolecular $n \rightarrow \rho^*$ and $\rho \rightarrow \rho^*$ charge transfer transitions (table 1). Intense absorption bands ($\epsilon \sim 10^4$) appear in the range 420–455 for the complexes which may be assigned to $d(\text{Fe}) \rightarrow \rho^*$ (ligand) charge transfer transitions. A broad weak band ($\epsilon = 270\text{--}700 \text{M}^{-1} \text{cm}^{-1}$) is observed at 620–690 nm.

3.4 Cyclic voltammetry

Cyclic voltammetric data are given in table 2. $[\text{Fe}(\text{RaaiR}')_3]\text{I}_2$ shows two redox responses at positive to SCE. One of them at higher positive potential ($E_{1/2}^M = 0.8\text{--}0.9 \text{V}$ vs SCE) exhibits cathodic peak on scan reversal while the second response at lower potential (E_{pc} 0.6 V) does not show reasonable E_{pc} on scan reversal (figure 1). The quasireversibility of voltammogram at 0.8–0.9 V is reflected in peak-to-peak separation ($\Delta E_p > 120 \text{mV}$). There are two redox active centres that may be oxidized: they are Fe(II) and I^- . To assign the redox responses we draw a cyclic voltammogram of $[\text{Fe}(\text{MeaaiMe})_3](\text{PF}_6)_2$ under identical experimental condition which does not show anodic response at 0.6 V and shows only quasireversible redox couple at 0.8–0.9 V. The latter couple has been assigned to the Fe(III)/Fe(II) couple (1), and the E_{pa} at 0.6 V corresponds to $\frac{1}{2}\text{I}_2/\text{I}^-$ reaction (2).

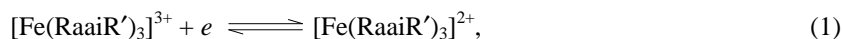


Table 1. Microanalytical^a and UV-Vis^b spectra data.

Compound	Found (calcd.) (%)				I_{\max}/nm ($10^{-3} \text{ e}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
	C	H	N	Fe	
[Fe(HaaiMe) ₃]I ₂ (3a)	41.51 (41.48)	3.48 (3.45)	19.41 (19.36)	6.7 (6.43)	622 (0.708), 422 (6.82) ^c , 358 (8.768), 302 (9.388), 226 (17.98)
[Fe(MeaaiMe) ₃]I ₂ (3b)	43.43 (43.53)	3.52 (3.95)	18.24 (18.46)	6.18 (6.13)	626 (0.518), 420 (9.35) ^c , 384 (12.78) ^c , 354 (11.00), 294 (7.07), 234 (12.86)
[Fe(ClaaiMe) ₃]I ₂ (3c)	37.12 (37.01)	2.98 (2.77)	17.47 (17.27)	5.92 (5.74)	690 (0.586), 418 (9.265) ^c , 378 (3.516) ^c , 368 (35.56), 284 (4.96) ^c , 242 (13.65) ^c
[Fe(HaaiEt) ₃]I ₂ (4a)	43.24 (43.53)	4.1 (3.96)	18.35 (18.47)	6.15 (6.13)	624 (3.89), 446 (3.17), 420 (5.85) ^c , 374 (11.56), 294 (8.426)
[Fe(MeaaiEt) ₃]I ₂ (4b)	45.18 (45.39)	4.12 (4.41)	17.74 (17.65)	6.1 (5.86)	624 (3.374), 424 (7.51) ^c , 380 (12.712), 374 (12.651), 294 (6.537)
[Fe(ClaaiEt) ₃]I ₂ (4c)	39.11 (39.02)	3.41 (3.25)	16.71 (16.56)	5.7 (5.50)	643 (0.265), 450 (4.54), 382 (42.53) ^c , 372 (43.79), 288 (6.507) ^c , 242 (13.93), 226 (20.617)

^aCalculated values are in parentheses; ^bsolvent MeCN; ^cshoulder

Table 2. Cyclic voltammetric^a data.

Compound	$E_{1/2}[\text{Fe(III)/Fe(II)}]$ (V) (ΔE_p , mV)	Ligand reductions (V)
[Fe(HaaiMe) ₃]I ₂ (3a)	0.878 (120)	-0.40 (110), -0.73 (120)
[Fe(MeaaiMe) ₃]I ₂ (3b)	0.815 (125)	-0.48 (110), -0.81 (130)
[Fe(ClaaiMe) ₃]I ₂ (3c)	0.805 (75)	-0.70 (140), -0.40 (130)
[Fe(HaaiEt) ₃]I ₂ (4a)	0.842 (85)	-0.44 (130), -0.78 (140)
[Fe(MeaaiEt) ₃]I ₂ (4b)	0.788 (80)	-0.52 (130), -0.88 (140)
[Fe(ClaaiEt) ₃]I ₂ (4c)	0.896 (90)	-0.42 (120), -0.75 (125)

^aSolvent MeCN; Pt-disk working electrode for **3**, **4**; reference SCE; supporting electrolyte [Bu₄N][ClO₄]. $E_{1/2} = 0.5 (E_{pa} + E_{pc})$, V; $\Delta E_p = (E_{pa} - E_{pc})$, mV, E_{pa} = anodic peak potential; E_{pc} = cathodic peak potential

Owing to charge transfer between I^- and $[\text{Fe}(\text{RaaiR}')_3]^{2+}$ in the ionic association and solvation effect, $1/2 \text{I}_2/\text{I}^-$ oxidation couple may be shifted to higher potential values compared to standard reported potential values.⁵⁴ The one-electron nature of the redox process in (1) is supported by the i_{pa}/i_{pc} (i_{pa} = anodic peak current and i_{pc} = cathodic peak current) which varies from 0.9–1.05 and on the comparing current height of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple.

There are three redox couples that appear at negative values to SCE and are due to reductions of the ligand (figure 1). Arylazoimidazoles usually accommodate two electrons at LUMO which is mostly azo in character. These three redox responses are due to azo^-/azo redox reaction of three-coordinated RaaiR' .^{32–36} Other three reductions were not observable because of

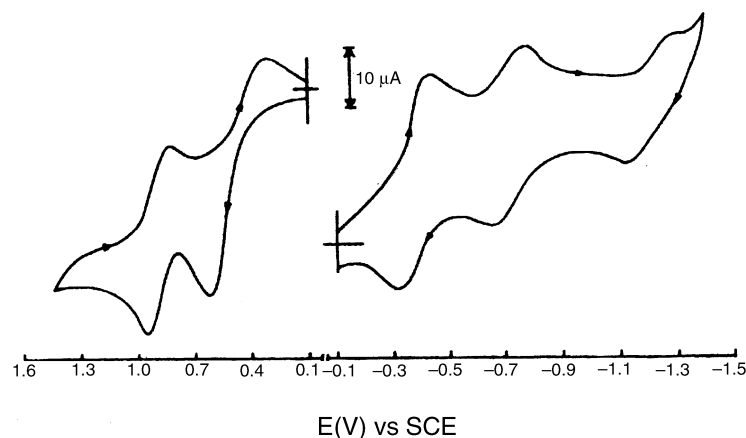
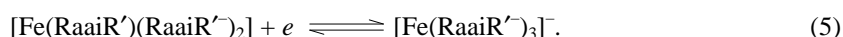
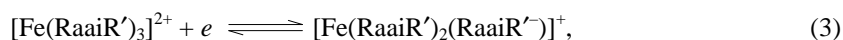


Figure 1. Cyclic voltammogram of $[\text{Fe}(\text{HaaiMe}_3)_2]\text{I}_2$ (**3a**) in MeCN.



The solvent cut-off region appears near -1.5 V. They certainly need more negative potential since electron are accommodated at SOMO which feels repulsion by incoming electron(s). Redox couples are systematically affected by substituents R and are linearly related to the Hammett s .

4. Conclusions

This work describes the coordination chemistry of iron(II) with the 1-alkyl-2-(arylo)imidazole ligand which contains the azoimine ($-\text{N}=\text{N}-\text{C}=\text{N}-$) function. The complexes have been synthesized and characterized by microanalytical, spectral, electrochemical and magnetic study.

Acknowledgement

Financial support from the University Grants Commission (UGC) is gratefully acknowledged. One of us (UR) thanks the UGC for a fellowship.

References

1. Raghavendra B S and Chakravorty A 1976 *Inorg. Chim. Acta.* **A14** 166
2. Krause R A and Krause K 1980 *Inorg. Chem.* **19** 2600
3. Krause R A and Krause K 1982 *Inorg. Chem.* **21** 1714
4. Ferreira V and Krause R A 1988 *Inorg. Chim. Acta* **145** 29
5. Goswami S, Chakravarty A R and Chakravorty A 1981 *Inorg. Chem.* **20** 2246
6. Goswami S, Chakravarty A R and Chakravorty A 1982 *Inorg. Chem.* **21** 2737
7. Goswami S, Chakravarty A R and Chakravorty A 1983 *Inorg. Chem.* **22** 602
8. Goswami S, Mukherjee R and Chakravorty A 1983 *Inorg. Chem.* **22** 2825
9. Datta D and Chakravorty A 1983 *Inorg. Chem.* **22** 1085
10. Ghosh B K and Chakravorty A 1989 *Coord. Chem. Rev.* **95** 239

11. Moreno J M, Ruiz J, Dominguez-Vera J M, Colacio E, Galisto D and Kivekas R 1994 *Polyhedron* **13** 203
12. Hayami S, Inone K, Osaki S and Maeda Y 1998 *Chem. Lett.* 987
13. Au Y-K, Cheung K-K and Wong W-T 1995 *Inorg. Chim. Acta* **238** 193
14. Hartmann H, Scheiring T, Fielder J and Kaim W 2000 *J. Organomet. Chem.* **604** 267
15. Fees J, Hausen H-D and Kaim W 1995 *Z. Naturforsch.* **B50** 15
16. Pramanik K, Shivakumar M, Ghosh P and Chakravorty A 2000 *Inorg. Chem.* **39** 195
17. Shivakumar M, Pramanik K, Bhattacharyya I and Chakravorty A 2000 *Inorg. Chem.* **39** 4332
18. Shivakumar M, Gangopadhyay J and Chakravorty A 2001 *Polyhedron* **20** 2089
19. Hotze A C G, Broekhuizen M E T, Velders A H, Vander Schilden K, Haasnoot J G and Reedijk J 2002 *Eur. J. Inorg. Chem.* 369
20. Saha A, Majumdar P, Peng S-M and Goswami S 2000 *Eur. J. Inorg. Chem.* 2631
21. Das C, Peng S-M, Lee G H and Goswami S 2002 *New J. Chem.* **26** 222
22. Mondal B, Paul H, Puranik P G and Lahiri G K 2001 *J. Chem. Soc., Dalton Trans.* 481
23. Pramanik N C, Pramanik K, Ghosh P and Bhattacharyya S 1998 *Polyhedron* **17** 1525
24. Bhattacharyya S, Chakraborty I, Dirghangi B K and Chakravorty A 2000 *Chem. Commun.* 1813
25. Bhattacharyya S, Chakraborty I, Dirghangi B K and Chakravorty A 2001 *Inorg. Chem.* **40** 286
26. Ghosh B K, Mukhopadhyay A, Goswami S, Ray S and Chakravorty A 1984 *Inorg. Chem.* **23** 4633
27. Das A, Peng S-M and Bhattacharyya S 2000 *Polyhedron* **19** 1227
28. Santra B K and Lahiri G K 1997 *J. Chem. Soc., Dalton Trans.* 129
29. Santra B K, Munshi P, Das G, Bharadwaj P and Lahiri G K 1999 *Polyhedron* **18** 617
30. Misra T K, Das D and Sinha C 1997 *Polyhedron* **16** 4163
31. Das D, Misra T K and Sinha C 1998 *Transition Met. Chem.* **23** 73
32. Misra T K, Das D, Sinha C, Ghosh P K and Pal C K 1998 *Inorg. Chem.* **37** 1672
33. Misra T K and Sinha C 1999 *Transition Met. Chem.* **24** 172
34. Pal S, Misra T K and Sinha C 2000 *Transition Met. Chem.* **25** 333
35. Pal S, Misra T K, Chattopadhyay P and Sinha C 1999 *Proc. Indian Acad. Sci. (Chem. Sci.)* **111** 687
36. Byabartta P, Pal S, Misra T K, Sinha C, Liao F-L, Pannerselvam K and Lu T-H 2002 *J. Coord. Chem.* **55** 479
37. Das D and Sinha C 1998 *Transition Met. Chem.* **23** 517
38. Pal S, Das D, Sinha C and Kennard C H L 2001 *Inorg. Chim. Acta* **313** 21
39. Rauth G K, Pal S, Das D and Sinha C 2001 *Transition Met. Chem.* **26** 679
40. Das D, Das A K and Sinha C 1999 *Anal. Lett.* **32** 567; Das D, Das A K and Sinha C 1999 *Talanta* **48** 1013
41. Santra P K, Das D, Misra T K, Roy R, Sinha C and Peng S-M 1999 *Polyhedron* **18** 1909
42. Santra P K, Misra T K, Das D, Sinha C, Slawin A M Z and Woollins J D 1999 *Polyhedron* **18** 2869
43. Santra P K, Sinha C, Sheen W-J, Liao F-L and Lu T-H 2001 *Polyhedron* **20** 599
44. Senapati S, Ray U S, Santra P K, Sinha C, Woollins J D and Slawin A M Z 2002 *Polyhedron* **21** 753
45. Akasaka T, Otsuki J and Araki K 2002 *Chem. Eur. J.* 130
46. Camalli M, Caruso F, Mattogno G and Rivarola E 1990 *Inorg. Chim. Acta* **170** 225
47. Nag J K, Santra P K, Sinha C, Liao F-L and Lu T-H 2001 *Polyhedron* **20** 2253
48. Bag K, De N K, De B B and Sinha C 1997 *Proc. Indian Acad. Sci. (Chem. Sci.)* **109** 159
49. Rypniewski W R, Managani S, Bruni S, Orioli P L, Casati M and Wilson K 1995 *J. Mol. Biol.* **251** 282
50. Wang L, Bailly C, Kumar A, Ding D, Bajic M and Wilson W D 2002 *Proc. Natl. Acad. Sci. USA* **97** 12
51. Bađ H, Trker A R, Tunceli A and Lale M 2001 *Anal. Sci.* **17** 901
52. Byabartta P, Dinda J, Santra P K, Sinha C, Pannerselvam K, Liao F-L and Lu T-H 2001 *J. Chem. Soc., Dalton Trans.* 2825
53. Bera P, Saha N, Kumar S, Banerjee D and Bhattacharya R 1999 *Transition Met. Chem.* **24** 425
54. Rubinson J F, Rubinson K A 1998 *Contemporary chemical analysis* (Englewood Cliffs, NJ: Prentice Hall)