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Mononuclear iron(III)macrocyclic complexes derived from 4-methyl-2,6-di(formyl/benzoyl)phenol and diamines: synthesis, spectral speciation and electrochemical behaviour

Sushil K. Gupta *, Yogendra S. Kushwah

School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India Received 5 February 2001; accepted 27 March 2001

Dedicated to Professor B.L. Khandelwal on the occasion of his 64th birthday

Abstract

Two series of macrocyclic iron(III) complexes of stoichiometry [Fe(L)Cl₂]Cl (1, 2) have been synthesised and characterised. Compounds belonging to series 1 are derived from 4-methyl-2,6-diformylphenol and diamines (H₂L), and those of 2 from 4-methyl-2,6-dibenzoylphenol and diamines. All the brown complexes have been characterised by physicochemical techniques. The mass, infrared, electronic, ESR and Mössbauer spectroscopies, magnetic susceptibility data, molar conductance, X-ray diffraction and cyclic voltammetric studies provide unambiguous evidence that 1 and 2 are high-spin iron(III) complexes in which the metal has an octahedral geometry. The Mössbauer data are consistent with high-spin iron(III) and substantial covalency in the Fe(III)–ligand bonds. Cyclic voltammetric studies in DMSO of the mononuclear iron(III) complexes show that they undergo quasi-reversible reduction with $E_{1/2}$ approximately -0.74 V versus SCE. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Iron(III) complexes; High-spin; Unsaturated macrocyclic ligand; ESR; Mössbauer; Powder XRD; Cyclic voltammetry

1. Introduction

Binuclear metal complexes of the unsaturated tetraaza diphenol (H₂L) and its derivatives have been the focus of extensive studies [1-3], but the mononuclear Fe(III) complexes have received little attention [4]. Iron-containing systems have great industrial and biological importance [5]; e.g. iron macrocyclic complexes have shown great potential recently as catalysts for the hydroxylation of alkanes [6]. Earlier we reported some mononuclear oxovanadium(IV) [7], Cu(II) [8] and Ni(II) [9] complexes with unsaturated macrocycles derived from the [2+2] template condensation of 4methyl-2,6-di(formyl/benzoyl) phenol with various diamines in the presence of metal ions. In continuation of our studies, we report herein the synthesis, characterisation and electrochemical behaviour of the mononuclear high-spin Fe(III) macrocyclic complexes.

2. Experimental

2.1. Materials and methods

All the chemicals used were of reagent grade and were used as received. Published methods [10,11] were used to synthesise 4-methyl-2,6-diformylphenol and 4-methyl-2,6-dibenzoylphenol. Ethylenediamine, 1,3-di-aminopropane *o*-phenylenediamine and ferric chloride were obtained from Aldrich and Merck. Solvents were purified by standard methods [12].

2.2. Preparation of the macrocyclic ligands

The macrocyclic ligands (H_2L) were synthesised by the condensation of 4-methyl-2,6-di(formyl/benzoyl) phenol with the appropriate diamines in 2:2 molar ratios by a modified literature method [13]. They showed satisfactory melting points and elemental analyses.

^{*} Corresponding author.

E-mail address: drskgcy@sancharnet.in (S.K. Gupta).





$[R = H(1), Ph(2); X = C_2H_4(a), 1, 3-C_3H_6(b), C_6H_4(c)]$

2.2.1. Template synthesis of complexes [Fe(L)Cl₂]Cl (1a-1c)

To a boiling solution of FeCl₃ (2 mmol) and 4methyl-2,6-diformyl phenol (0.45 g, 4 mmol) in ethanol (20 cm³), an ethanolic solution of the diamine (4 mmol) [ethylenediamine (**a**), 1,3-diaminopropane (**b**) and *o*phenylenediamine (**c**)] was added slowly with constant stirring and the mixture was boiled under reflux for 4 h when a brown compound separated out. The product was filtered out, washed with ethanol and dried in air. The yields were 70-78%.

The complexes were also prepared by heating a 1:2 mixture of $FeCl_3$ and ligand H_2L in EtOH.

1a. Anal. Found: C, 48.71; H, 4.40; Cl, 19.40; N, 10.59. Calc. for C₂₂H₂₄N₄O₂Cl₃Fe: C, 49.05; H, 4.49; Cl, 19.74; N, 10.4%. FAB MS; m/z (%): 503(1) $[M]^+$, 469(5) $[MH - Cl]^+$, 432(15) $[MH - 2Cl]^+$, 154(100). IR (cm⁻¹): v(Fe–Cl) 319, v(C...O) 1548, v(C=N) 1630, 1652, v(N–H) 3187. $\mu_{\rm eff}$ (BM) at room temperature (r.t.): 5.94. UV–Vis (nm) (ε , M⁻¹ cm⁻¹) (DMSO): 519(2620), 444(3.9 × 10³), 375(1.04 × 10⁴), 330(9.7 × 10³), 267(2.05 × 10⁴). ESR (DMSO, r.t.): g 2.014. Mössbauer (δ , mm s⁻¹; $\Delta E_{\rm Q}$, mm s⁻¹, r.t.): 0.295; 0.665. CV data: $E_{1/2}$ (V) – 0.768; $\Delta E_{\rm p}$ (mV) 208. $\Lambda_{\rm M}$ (Ω^{-1} cm² mol⁻¹) (10⁻³ M, DMSO, 25°C): 59.

1b. Anal. Found: C, 50.60; H, 4.80; Cl, 18.40; N, 10.21. Calc. for $C_{24}H_{28}N_4O_2Cl_3Fe:$ C, 50.86; H, 4.97; Cl, 18.76; N, 9.88%. FAB MS; m/z (%): 531(1) $[M]^+$, 496(5.3) $[M - Cl]^+$, 459(12) $[M - 2Cl]^+$, 154(100). IR

(cm⁻¹): v(Fe–Cl) 312, v(C...O) 1551, v(C=N) 1629, 1656, v(N–H) 3080. $\mu_{\rm eff}$ (BM) at r.t.: 5.60. UV–Vis (nm) (ε , M⁻¹ cm⁻¹) (DMSO): 523(3240), 451(3.0 × 10³), 371(1.1 × 10⁴), 328(8.4 × 10³), 266(2.0 × 10⁴). ESR (DMSO, r.t.): g 2.014. Mössbauer (δ , mm s⁻¹; $\Delta E_{\rm Q}$, mm s⁻¹, r.t.): 0.308; 0.722. CV data: $E_{1/2}$ (V) – 0.764; $\Delta E_{\rm p}$ (mV) 208. $\Lambda_{\rm M}$ (Ω^{-1} cm² mol⁻¹) (10⁻³ M, DMSO, 25°C): 70.

1c. Anal. Found: C, 56.46; H, 3.75; Cl, 16.40; N, 8.61. Calc. for C₃₀H₂₄N₄O₂Cl₃Fe: C, 56.76; H, 3.81; Cl, 16.75; N, 8.82%. FAB MS; m/z (%): 599(1.3) $[M]^+$, 562(11) $[M - Cl]^+$, 527(7.2) $[M - 2Cl]^+$, 154(100). IR (cm⁻¹): v(Fe-Cl) 305, v(C...O) 1535, v(C=N) 1621, 1650, v(N-H) 3072. μ_{eff} (BM) at r.t.: 6.40. UV–Vis (nm) (ε , M⁻¹ cm⁻¹) (DMSO): 495(1510), 444(8.07 × 10³), 285(1.1 × 10⁴), 266(1.6 × 10⁴). ESR (DMSO, r.t.): g 2.013. Mössbauer (δ , mm s⁻¹; ΔE_Q , mm s⁻¹, r.t.): 0.173; 0.722. CV data: $E_{1/2}$ (V) – 0.653; ΔE_p (mV) 161. Λ_{M} (Ω^{-1} cm² mol⁻¹) (10⁻³ M, DMSO, 25°C): 56.

2.2.2. Template synthesis of complexes [Fe(L')Cl₂]Cl (2a-2c)

These complexes were prepared by a similar procedure as described above, employing 4-methyl-2,6-dibenzoyl phenol and diamines in the presence of FeCl₃ in a 2:2:1 ratio in 75-80% yields.

2a. Anal. Found: C, 65.25; H, 4.70; Cl, 12.80; N, 6.51. Calc. for C₄₆H₄₀N₄O₂Cl₃Fe: C, 65.53; H, 4.78; Cl, 12.61; N, 6.64%. IR (cm⁻¹): v(Fe–Cl) 315, v(C—O) 1508, v(C=N) 1595, 1640, v(N–H) 3190. μ_{eff} (BM): 6.30. ESR (polycrystalline, r.t.): g 2.00. Mössbauer (δ , mm s⁻¹; ΔE_{o} , mm s⁻¹, r.t.): 0.291; 0.563.

2b. Anal. Found: C, 66.40; H, 4.98; Cl, 12.56; N, 6.67. Calc. for C₄₈H₄₄N₄O₂Cl₃Fe: C, 66.18; H, 5.09; Cl, 12.20; N, 6.43%. FAB MS: m/z (%) 835(1) $[M]^+$, 800(6) $[M - Cl]^+$, 763(5) $[M - 2Cl]^+$, 578(100). IR (cm⁻¹): v(Fe–Cl) 310, v(C.O) 1548, v(C=N) 1599, 1632, v(N–H) 3109. $\mu_{\rm eff}$ (BM) at r.t.: 6.4. ESR (polycrystalline, r.t.): g 2.00. Mössbauer (δ , mm s⁻¹; $\Delta E_{\rm Q}$, mm s⁻¹, r.t.): 0.290; 0.595.

2c. Anal. Found: C, 68.82; H, 4.35; Cl, 11.68; N, 6.21. Calc. for $C_{54}H_{40}N_4O_2Cl_3Fe:$ C, 69.06; H, 4.29; Cl, 11.32; N, 5.96%. IR (cm⁻¹): v(Fe–Cl) 318, v(C...O) 1532, v(C=N) 1606, 1648, v(N–H) 3147. μ_{eff} (BM) at r.t.: 6.01. UV–Vis (nm) (ε , M⁻¹ cm⁻¹) (DMSO): 570(2050), 459(5.780 × 10³), 348(2.8 × 10⁴), 297(4.9 × 10⁴), 267(4.08 × 10⁴). ESR (DMSO, r.t.): *g* 1.986. Mössbauer (δ , mm s⁻¹; ΔE_Q , mm s⁻¹, r.t.): 0.289; 0.570. CV data: $E_{1/2}$ (V) – 0.792; ΔE_p (mV) 213. Λ_M (Ω^{-1} cm² mol⁻¹) (10⁻³ M, DMSO, 25°C): 55.

2.3. Physical measurements

The IR spectra (4000–200 cm⁻¹) were recorded on a Perkin–Elmer 883 spectrophotometer with KBr/CsI pellets. The electronic spectra in DMSO solution were obtained with a Shimadzu UV-160A recording spectrophotometer. The ESR spectra in the polycrystalline state and in DMSO solution were recorded on a Varian E-112 spectrometer in the X-band region at r.t. Room temperature magnetic susceptibility measurements were performed with an EG and G PAR155 vibrating sample magnetometer. The effective magnetic moments were calculated using the formula $\mu_{eff} = 2.828$ $(\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. The diamagnetic contributions were calculated by using literature tabulations [14]. The FAB masses in the positive mode were recorded on a VG Autospec mass spectrometer. *m*-Nitrobenzyl alcohol (*m*-NOBA) was used as the matrix.

The X-ray powder diffraction patterns for the complexes were recorded on a Rigaku 'Rotaflex' RU 200 rotating anode X-ray diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å) with angular range 10–90°.

Mössbauer spectral measurements were made on a constant-acceleration spectrometer calibrated with metallic iron at r.t. All isomer shifts are reported with respect to the r.t. iron(0) transmission spectrum. The observed spectra were computer-fitted using Lorentzian lines and a least-squares minimisation technique.

2.4. Electrochemical experiments

All the measurements were performed under a nitrogen atmosphere in DMSO at r.t. Solutions contained 10^{-4} mol dm⁻³ of the complex and 0.1 mol dm⁻³ of TEAP (tetraethylammoniumperchlorate) as the supporting electrolyte. Scan speeds of 50-200 mV s⁻¹ were employed. Cyclic voltammograms were run on an EG and G Versastat II system. The three-electrode measurements were carried out with a platinum electrode in conjunction with a Pt wire auxilliary electrode and a saturated calomel electrode (SCE) as the reference electrode. The electrode performance was monitored by observing the ferrocenium/ferrocene (Fc⁺/Fc) couple in the above solvent system.

Constant-potential electrolyses were carried out on the same equipment. Conductivity measurements were done with a Global DCM 900 digital conductivity meter with a solvent concentration of 1 mM. Elemental



Scheme 1.

analyses were obtained on a Carlo Erba 1100 elemental analyser.

3. Results and disscusion

3.1. Synthesis

The template condensation of 4-methyl-2,6-di(formyl/benzoyl)phenol with various diamines in the presence of FeCl₃ in ethanol (Scheme 1) yields light and dark brown complexes of composition [Fe(L)Cl₂]Cl (1,2). All the complexes are stable at room temperature, soluble in MeOH, DMSO and DMF (except **2a** and **2b**), and melt with decomposition at 230–280°C. The molar conductance measurements support the formulation [Fe(L)Cl₂]Cl as a 1:1 electrolyte [15]. The elemental analyses were in the agreement with the above formulations and rule out the possibility that the complexes should be formulated as [Fe(L)Cl₂][FeCl₄]. Thin layer chromatographic analysis confirmed the purity of the complexes.

3.2. Mass spectra

The FAB positive-mass spectra of the Fe(III) cationic complexes (EI for **2b**) obtained by using *m*-NOBA as matrix [16–18] show molecular ion peaks [Fe(L)Cl₂]⁺ in all the complexes. The other fragments exhibit features due to $[M - Cl]^+$, $[M - 2Cl]^+$. For ions containing Cl peaks, $M - Cl^{35}$ and $M - Cl^{37}$ were observed. The other peaks at 154 and 136 are due to the NBA matrix. The calculated and observed isotropic patterns are in good agreement. The mass spectra of complexes **2a** and **2c** could not be recorded due to insufficient volatility.

3.3. FT IR spectra

The IR spectra of the ligands show weak broad bands at 2600-2850 cm⁻¹. These bands can be ascribed to O-H stretching vibrations, which are known to shift significantly to lower frequencies as a result of OH…N intra-molecular bonding [19-21]. Very strong bands at 1270 cm⁻¹ were assigned to in-plane bending (O-H) vibrations of the ligands. The absence of O-H stretching and $\delta(O-H)$ vibration in the spectra of the complexes indicated deprotonation of the -OH groups [19]. The bands observed in the region 3072-3190 cm⁻¹ in the complex are assigned to N-H stretching. The low value of v(N-H) is attributed to hydrogen bonding. The presence of C=N stretching vibrations in the spectra of the complexes 1 around 1626 and 1650 cm^{-1} and in 2 around 1600 and 1640 $cm^{-1}suggests$ that only one arm of the formyl/benzoval group of the phenolic unit is involved in coordination. The bands at

1626 in **1** and 1600 cm⁻¹ in **2** are at a frequency lower by approximately 11 and 15 cm⁻¹, respectively, than those in the free ligands. This can be ascribed to the withdrawn of electron density from the nitrogen atom owing to coordination. The band observed at approximately 1550 cm^{-1} has been assigned due to the $v(C \cdots O)$ vibrations of the phenol [22] as a consequence of the delocalisation of double bond in the chelate rings that has increased the bond order of the phenolic C–O. The absorption bands in the 305-319 cm⁻¹ region are assignable to v(Fe-Cl) vibrations characteristic of terminal chlorine in trans configurations in an octahedral arrangement of the metal ion [23]. Even in the cases of 1c and 2c, a *trans* configuration seems more likely because of the similarity of the data to those of the a and **b** series.

3.4. Magnetic properties

The magnetic susceptibility data of all the Fe(III) complexes were determined in the solid state at room temperature. The magnetic moments (Section 2) for all the Fe(III) complexes lie in the range 5.70–6.40 BM. The experimental μ_{eff} data match those for other d⁵ Fe(III) complexes. This is apparent from the ground state of the Fe(III) ion, which in the weak octahedral field gives a ${}^{6}A_{1g}$ ground state that has no orbital angular momentum.

3.5. Electronic spectra

The d-d transitions in high-spin Fe(III) complexes are spin forbidden and hence weak. The high-spin octahedral Fe(III) complexes are expected to show four absorption bands in the electronic spectra corresponding to the transitions: ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$; ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$; ${}^{6}A_{1g} \rightarrow$ $\{{}^{4}E_{g}, {}^{4}A_{1g}\}$; ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (D) [24]. In the present investigation the Fe(III) complexes in DMSO exhibit intense absorptions in the visible region. These low energy transitions are ascribed to ligand-to-metal charge transfer because of their large extinction coefficients and the fact that the metal ion is more easily reduced than oxidised. This is consistent with the cyclic voltammetric studies (see Section 4). In addition, all the complexes show very intense absorptions in the UV region, possibly due to intra-ligand transitions as observed in the free ligands at similar energies.

3.6. ESR spectra

The room temperature ESR spectra in DMSO of 1a-1c and 2c, and in the polycrystalline state of 2a, 2b show transitions centred at g = 2.00. This may be attributed to the extremely small spin orbital coupling

[25]. This fact also allows easy observation of the ESR spectrum at room temperature.

3.7. Mössbauer spectroscopy

Iron-57 Mössbauer spectroscopy was utilised to provide a direct probe of the electronic and chemical environments of the mononuclear iron(III) sites in these complexes. Zero-field Mössbauer spectra of 1 and 2 at 300 K are shown in Fig. 1. Each spectrum consists of a single quadrupole-split doublet, the two lines being of unequal intensity. The asymmetric line broadening may be attributed to slow spin-lattice relaxation [26], but in the absence of spectra at low temperatures it is impossible to confirm this. While comparing the values (ΔE_{Ω}) of the quadrupole-splitting for these two types of complexes, it appears that the iron site in complex 2 (ca. 0.576 mm s^{-1}) is more symmetric than that in complex 1 (ca. 0.703 mm s⁻¹). The values of the isomer shifts (δ) are in the range 0.173–0.308 mm s⁻¹, less than the values reported $(0.40-0.70 \text{ mm s}^{-1})$ for high-spin iron(III) octahedral complexes [27]. This indicates a higher s-electron density at iron possibly due to the higher covalent character of the bond to iron and/or reduced d-electron density at iron(III) resulting in deshielding of the s-electrons [28].

3.8. X-ray diffraction

The X-ray powder diffraction patterns of the complexes (Table 1) show them to be crystalline. However, efforts to grow single crystals did not succeed and this precluded a single crystal X-ray determination.

Thus, following the analytical and spectral evidence, complexes 1 and 2 can be assigned a monomeric octahedral geometry around iron with FeN_2O_2 cores and two chlorines in the *trans* position. The proposed structure of these complexes is shown in Fig. 1.



R, R = H(1) or Ph(2); X = $C_2H_4(a)$; 1,3- $C_3H_6(b)$; $C_6H_4(c)$



Fig. 1. Zero-field ⁵⁷Fe Mössbauer spectra of complexes 1a, 1b and 2a-2c at 300 K, referenced to iron metal.

4. Electrochemistry

4.1. Cyclic voltammetry

The electrochemical behaviour of the unsaturated macrocyclic complexes 1a-1c and 2c has been studied by cyclic voltammetry (CV) in DMSO using a Pt electrode under dry nitrogen atmosphere at room tem-

perature. Fig. 2 shows the cyclic voltammograms of complexes 1a and 1b. All the complexes exhibit quasireversible Fe(III)/Fe(II) reduction waves ($E_{1/2} = -$ 0.653 to -0.792 V) at a scan rate of 50 mV s⁻¹ with a peak-to-peak width much larger than that observed for the one-electron couple Fc⁺/Fc ion in the same solvent under the same experimental conditions ($E_{1/2} =$ 0.5($E_{p,c} + E_{p,a}$) = 0.48 V and $\Delta E_p = E_{p,c} - E_{p,a} = 80$ mV). The observed $E_{1/2}$ values for these couples are in good agreement with the reported value [29]. The $E_{1/2}$ value for **2c** is more negative than those for series **1**;

Table 1

The main bands in the X-ray diffraction powder patterns of the complexes

Complex	d lines ^a (Å)
[Fe(L _a)Cl ₂]Cl	5.68(6), 4.43(7), 3.47(100), 3.35(82), 3.26(53),
(1a)	2.99(80), 2.96(51), 2.72(26), 2.63(39), 2.09(21),
	1.88(11), 1.59(12)
[Fe(L _b)Cl ₂]Cl	5.27(24), 4.30(23), 4.20(51), 3.79(47), 3.65(100),
(1b)	3.33(38), 2.93(39), 2.82(26), 2.36(30), 1.95(14),
	1.88(12), 1.72(12)
[Fe(L _c)Cl ₂]Cl	8.11(73), 7.56(63), 6.79(41), 6.21(44), 5.91(42),
(1c)	5.00(46), 4.63(58), 4.33(50), 3.72(52), 3.23(100),
	2.03(25)
[Fe(L' _a)Cl ₂]Cl	3.48(100), 3.35(61), 3.26(51), 3.00(80), 2.96(44),
(2 a)	2.64(41), 2.08(39), 1.88(14), 1.6(13), 1.59(17)
[Fe(L' _b)Cl ₂]Cl	6.34(14), 5.26(12), 4.30(12), 4.19(71), 3.79(40),
(2b)	3.61(100), 3.33(53), 2.93(53), 2.40(46), 2.11(57),
	1.72(13), 1.50(19)
[Fe(L' _c)Cl ₂]Cl	8.46(100), 7.55(8), 6.95(5), 5.63(5), 4.55(6),
(2c)	3.44(14), 3.38(12), 2.81(12), 2.43(4), 1.89(2)

^a Intensities are given in parentheses.



Fig. 2. Cyclic voltammograms of complexes 1a and 1b (0.1 mM) in DMSO at 100 mV s⁻¹.

this can be ascribed to the electron-rich substituents at the 2,6-positions. The plot of cathodic peak current (i_{pc}) versus square root of scan rate $(v^{1/2})$ is nearly linear, indicative of quasi-reversible behaviour [30]. The peakto-peak separation (ΔE_p) increases at high scan rates, showing the quasi-reversible nature of the electron transfer process. Further, the ΔE_p values are greater than the Nernstian value $(\Delta E_p \cong 59 \text{ mV})$ for a one-electron reduction system. This indicates a considerable reorganisation of the coordination sphere during electron transfer. Controlled potential electrolysis for complex **1a** in DMSO solution at -0.90 V involved the passage of 0.97 equiv. of charge, indicating one-electron reduction of the mononuclear iron species.

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