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Some Iron(III) Complexes with Polydentate Schiff Base Ligands

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Abstract

The iron(III) complexes of three Schiff base ligands are studied as their chloride or perchlorate salts and their electronic spectra, EPR spectra, and electrochemical behavior reported. Two of these ligands are formed from reaction between salicylaldehyde and 9 or 12-membered tri- or tetraazalkanes. EPR evidence indicates that one of the complexes, [1,12-bis(2-hydroxybenzylidene)-(1,4,9,12-tetraazadodec-6-ene)iron(III)]perchlorate-1,5-water, is a spin-crossover species containing both high-spin and low-spin iron(III) in equilibrium. The third ligand comes from pyrrole-2-carboxaldehyde and a tetraazadodecane.

Introduction

Much of the interest in iron(III) Schiff base complexes is in their use as models for biological heme electron transfer [1–4], for the iron-binding site of lactoferrin [5], for the active site of the catechol-cleaving dioxygenases [6] and for other iron tyrosinate proteins [7]. They also have aspects of behavior similar to those of iron–porphyrin compounds [8]. The iron(III) complexes of salicylaldimine-type ligands are also intrinsically interesting because some of them exhibit spin-crossover transformations that are dependent on temperature. Spin transitions are believed to play an important role in biological systems. For example spin equilibria in some hemoproteins may be essential to electron transport [9]. The change in coordination geometry and metal–ligand bond length with change in spin state are interesting in both inorganic transition metal chemistry [10–13] and heme metalloprotein chemistry [9]. Complexes of this type are often prone to form oxo-bridged binuclear compounds so care must be exercised in their preparation to exclude water, to isolate the solid product soon after its formation and not allow it to remain in the solvent too long.

Ligands used in this study are shown in Fig. 1.

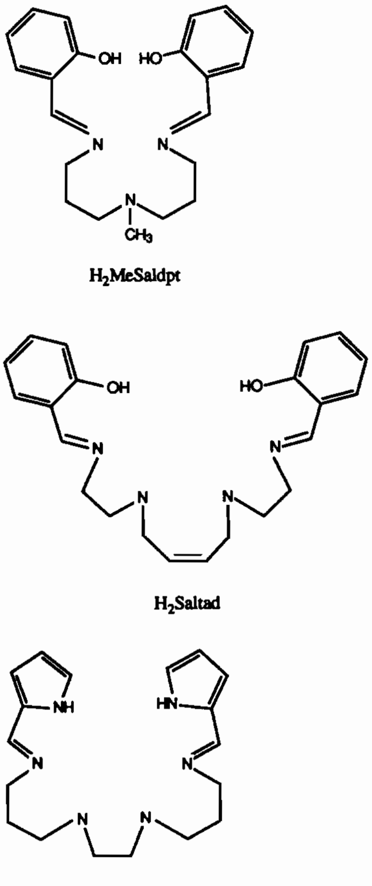

Fig. 1. Ligands used in this study.

Experimental

The UV–Vis spectra were obtained using a Perkin-Elmer Lambda 3B spectrophotometer. The data are reported as wavelength in nm (molar absorptivity in l mol^{-1} cm^{-1}). EPR was performed on a Varian E-12 X-band spectrometer calibrated with DPPH and $VO(Acac)_2$ near $g = 2$. g values are ± *ca.* 10^{-3} g^2.

Electrochemical measurements were made at 25 ± 0.2 °C in dimethylformamide (DMF) which had been distilled *in vacuo* (10 mm Hg) off CaH_2. The

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TABLE I. Absorption Spectra of Complexes[a]

Compound	Solvent								
Fe(CH_3Saldpt)Cl	CH_3OH		515(2.6)	405sh(2.5)	324(7.0)	303sh(5.6)	254sh(20.6)	237(27.4)	224sh(23.5)
Fe(Saltad)ClO_4	CH_3NO_2		505(1.9)		387(4.1)				
Fe(Pctad)ClO_4	CH_3NO_2	700(0.5)[b]	533(2.1)	447sh(1.3)	396(3.7)				

[a]Band positions in nm (10^{-3} × molar absorptivity, M^{-1} cm^{-1}). [b]Broad shoulder.

supporting electrolyte in all cases was tetraethylammonium perchlorate. The three-electrode cell configuration was controlled with a system comprising a PAR-173 potentiostat, a PAR-176 i/E converter, and a PAR-175 waveform generator. Potentials were measured with respect to the Ag^+ (0.01 M/0.1 M NEt_4ClO_4)/Ag electrode, which we have measured as being at +0.30 V *versus* a saturated calomel electrode in acetonitrile [14]. The potentials may thus be expressed with reference to the SHE by the addition of *ca.* 545 mV. Corrections for IR-drop were estimated from ΔE_p *versus* i_{pc} plots [15] for Nernstian $n = 1$ standards (*N,N,N',N'*-tetramethyl-*p*-phenylenediamine [16], and methyl viologen hexafluorophosphate [17]). A Beckman rotating platinum disc electrode (area 0.300 cm^2) was used for rotating disc (RPE) polarography and also as a stationary planar electrode for cyclic voltammetry. Microanalyses (C, H, N, S) were performed by Canadian Microanalytical Service Ltd. (Vancouver). Reagents for syntheses were used as received from Sigma and Aldrich.

Fe(MeSaldpt)Cl·3H₂O, [1,9-bis(2-hydroxybenzylidene)-(1,5,9-triazanonane)iron(III)]chloride-3-water

Salicylaldehyde (2.44 g, 20 mmol), 1,5,9-triazanonane (1.46 g, 10 mmol) and 4 ml of aqueous 5 N NaOH were combined in 30 ml of methanol and the solution was refluxed briefly. A methanol solution (20 ml) of iron(III) chloride (2.70 g, 10 mmol) was then added and the solution again refluxed briefly. The solution volume was reduced by half (rotary evaporation) and left overnight. The solvent was then decanted, leaving a purple gum which was recrystallized from ethanol and air-dried to give 2.20 g (50% yield) of dark purple crystals.

Anal. Calc. for $C_{21}H_{25}ClFeN_3O_2 \cdot 3H_2O$: C, 50.8; H, 6.29; N, 8.46. Found: C, 50.9; H, 5.96; N, 8.41%.

Fe(Saltad)(ClO₄)·1.5H₂O, [1,12-bis(2-hydroxybenzylidene)-(1,4,9,12-tetraazadodec-6-ene)-iron(III)] perchlorate-1.5-water

Salicylaldehyde (2.44 g, 20 mmol), 1,4,9,12-tetraazadodec-6-ene (1.72 g, 10 mmol), and 4 ml of aqueous 5 N NaOH were combined in 30 ml of methanol and the solution was refluxed briefly. A methanol solution (20 ml) of iron(III) perchlorate·$11H_2O$ (5.56 g, 10 mmol) was then added and the solution again refluxed briefly, resulting in the formation of a dark purple solid, which was filtered off, recrystallized from DMF and dried *in vacuo* (P_4O_{10}) to give 2.30 g (43% yield) of dark purple crystals.

Anal. Calc. for $C_{22}H_{24}ClFeN_4O_6 \cdot 1.5H_2O$: C, 47.3; H, 4.87; N, 10.1. Found: C, 47.6; H, 5.26; N, 10.2%.

Fe(Pctad)(ClO₄)·CH₃OH, [(1,5,8,12-Tetraazadodecane)bis(2-pyrrolidene)iron(III)]perchlorate-methanol

Pyrrole-2-carboxaldehyde (1.90 g, 20 mmol) and 1,5,8,12-tetaazadodecane (1.72 g, 10 mmol) were combined in 30 ml of methanol and 2 ml of trimethyl orthoformate were added. The solution was refluxed and a methanol solution (20 ml) of iron(III) perchlorate·$11H_2O$ (5.56 g, 10 mmol) containing 2 ml of trimethyl orthoformate was added slowly to the refluxing solution. After an hour of refluxing, the purple solid which had formed was filtered off and dried *in vacuo* (P_4O_{10}) to give 1.03 g (43% yield) of purple needles.

Anal. Calc. for $C_{18}H_{26}ClFeN_6O_4 \cdot CH_3OH$: C, 44.4; H, 5.89; N, 16.4. Found: C, 43.8; H, 5.81; N, 16.2%.

Results and Discussion

Electronic Spectra

The main feature of the electronic spectra of these compounds (see Table 1) is the relatively intense charge-transfer band in the 515–500 nm region, which can be assigned to a transition from the p_π orbital on the phenolate oxygen to the partially filled d_π orbitals on the iron [18]. These bands are supplemented by a shoulder at lower energy which is probably also due to charge-transfer. The bands in the 300–400 nm range are likely due to ligand π–π^* transitions [19].

EPR Spectroscopy

The compound Fe(MeSaldpt)Cl shows a signal at $g = 9.5$ when dissolved in DMF (see Table II). Further evidence of high-spin character for this compound is the signal at $g = 4.3$ in solid and solution at both ambient temperature and 77 K. A weak resonance at $g = 2.0$ in the solid state (at both tem-

TABLE II. Electron Paramagnetic Resonance of the Complexes

Compound	T (K), medium		g factors		
$Fe(CH_3Saldpt)Cl$	298, solid		4.25	2.13	1.98
	77, solid		4.22		1.98
	77, DMF	9.5	4.51	4.25	3.76
$Fe(Saltad)ClO_4$	298, solid		4.19	2.13	
	298, DMF			2.15	1.98
	77, solid		4.14	2.15	
	77, DMF		4.29	2.18	1.94
$Fe(Pctad)ClO_4$	298, solid			2.22	
	77, solid			2.29	1.8
	77, DMF		2.51	2.39	1.8

peratures) which disappears when the sample is dissolved in DMF is indicative of some low-spin impurity present in the solid phase.

The compound $Fe(Saltad)ClO_4$ shows bands at $g = 4.2$ and $g = 2.2$ at both room temperature and 77 K for samples which are in the solid state (see Fig. 2). However in solution only the $g = 2.2$ band is present at both temperatures. (The $g = 4.2$ resonance for the compound in solution at 77 K is very weak.) The $g = 4.2$ band is typical of rhombically distorted high-spin iron(III) [20], while $g = 2.2$ is characteristic of low-spin iron(III). The disappearance of the $g = 4.2$ resonance in solution is probably due simply to broadening of the band as the relaxation time increases. This appears to be a spin-crossover compound with both high-spin and low-spin iron(III) present at the temperatures studied.

The $Fe(Pctad)ClO_4$ complex has only a single resonance at $g = 2.3$ at ambient temperature which indicates that this compound is low-spin. The ligand in this complex is the pyrrole analogue of 1,14-bis(2-hydroxyphenyl)-2,6,9,13-tetraazadodecane [5] with pyrrole groups in place of the phenolate groups.

Electrochemistry

In the cyclic voltammetry of $Fe(MeSaldpt)^+$ (see Fig. 3) the peak current ratio (i_{pa}/i_{pc}) was close to unity for all scan rates (from 50 to 500 mV/s). A plot of peak potential separation (ΔE_p) *versus* cathodic peak current at varying scan rates gives a value of $\Delta E_p = 63$ (±11) in V at zero cathodic current

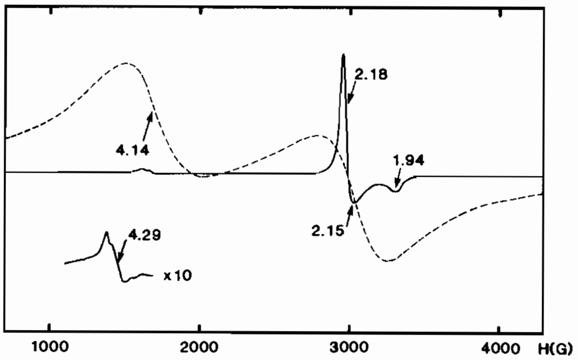

Fig. 2. EPR of $Fe(Saltad)ClO_4$ in DMF solution (——) and in the solid state (- - - -) at 77 K. (1 G = 10^{-4} T).

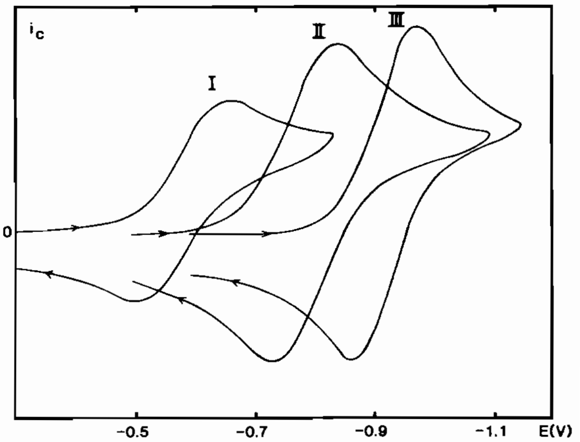

Fig. 3. Cyclic voltammograms of: I, $Fe(MeSaldpt)^+$; II, $Fe(Saltad)^+$; III, $Fe(Pctad)^+$; in DMF/NEt_4ClO_4 at a scan rate of 100 mV/s. Potentials are referred to the non-aqueous Ag^+/Ag electrode.

(see Table III); this is indicative of an electron transfer process that follows Nernstian behavior [15]. We assign this peak as being due to Fe(III)/Fe(II) reduction since the reduction potential for the similar complex, [bis[3-(3-methoxysalicylideneamine)propyl]-amino-*O*,*N*,*N*′,*N*″,*O*′](pyridine)-iron(III) tetraphenylborate, has been reported as +18 mV in dichloromethane with an SCE reference electrode [21]. No other electrochemical processes were observed in the potential range +1.0 to −2.0 V.

The reduction potential of $Fe(Saltad)^+$ is quite close to that of $[Fe(Sal)_2trien]^+$ (−0.79 *versus*

TABLE III. Redox Properties of the Complexes

Compound	Solvent	$E_{1/2}$ (mV)	ΔE_p (mV)^a	$10^6 \times D$	$10^8 \times D\eta$
$Fe(CH_3Saldpt)Cl$	DMF	−660	63(±11)	1.22	1.06
$Fe(Saltad)ClO_4$	DMF	−790	94(±2)	0.795	0.688
$Fe(Pctad)ClO_4$	DMF	−945	72(±3)	4.08	3.53

$^a\Delta E_p$ at zero i_{pc}.

-0.82 V) as studied by Kadish *et al.* [22]. The two ligands are very similar, the only difference being that the Saltad has four carbons and a double bond between the middle two amine nitrogens while the $(Sal)_2$trien has two sp_3-hybridized carbons in this place. The behavior of current ratio and peak potential separation indicates a quasi-reversible reduction process. EPR measurements indicate that this may be a spin-crossover compound, as both high-spin and low-spin species are present at room temperature. The rather low value measured for the limiting current at the rotating platinum electrode may thus arise from a kinetic phenomenon, if only one of the two species in equilibrium is being reduced at this potential.

For $Fe(Pctad)^+$ the limiting value of ΔE_p is 72(±3) mV at zero cathodic peak current. This deviation from the Nernstian value of 59 mV [16] indicates a non-reversible electron transfer. The increase of peak current ratio (i_{pa}/i_{pc}) with increase in scan rate (from 10 to 500 mV/s), approaching a limiting value of one, is indicative of a chemical reaction following the electron transfer [23], which could account for the non-Nernstian behavior. The following reaction is possibly dissociation of the complex subsequent to the reduction step.

References

1 K. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, New York, 1975.
2 D. T. Sawyer (ed.), *ACS Symp. Ser.*, No. 38 (1977).
3 A. W. Addison, W. R. Cullen, D. Dolphin and B. R. James (eds.), 'Biological Aspects of Inorganic Chemistry', Wiley, New York, 1977.
4 D. Dolphin (ed.), 'Porphyrins', Vols 1–IV, Academic Press, New York, 1978.
5 E. W. Ainscough, A. M. Brodie, J. E. Plowman, K. L. Brown, A. W. Addison and A. R. Gainsford, *Inorg. Chem., 19*, 3655 (1980).
6 R. H. Heistand, II, A. L. Roe and L. Que Jr., *Inorg. Chem., 21*, 676 (1982).
7 L. Casella, M. Gullotti, A. Pintar, L. Messori, A. Rockenbauer and M. Györ, *Inorg. Chem., 26*, 1031 (1987).
8 B. J. Kennedy, G. Brain, E. Horn, K. S. Murray and M. R. Snow, *Inorg. Chem., 24*, 1647 (1985).
9 E. V. Dose, M. F. Tweedle, L. J. Wilson and N. J. Sutin, *J. Am. Chem. Soc., 99*, 3887 (1977).
10 S. A. Cotton, *Coord. Chem. Rev., 8*, 185 (1972).
11 H. A. Goodwin, *Coord. Chem. Rev., 18*, 293 (1976).
12 J. D. Oliver, D. F. Mullica, B. B. Hutchinson and W. O. Milligan, *Inorg. Chem., 19*, 165 (1980).
13 B. A. Katz and C. E. Strouse, *Inorg. Chem., 19*, 658 (1980).
14 A. W. Addison and J. H. Stenhouse, *Inorg. Chem., 17*, 2161 (1978).
15 V. D. Parker, in A. J. Bard (ed.), 'Electroanalytical Chemistry', Vol. 14, Marcel Dekker, New York, p. 28.
16 S. Piekarski and R. N. Adams, in A. Weissberger and B. W. Rossiter (eds.), 'Techniques of Chemistry, Vol. I, Physical Methods of Chemistry, Part IIA Electrochemical Methods', Wiley, New York, 1971, p. 551.
17 U. Sakaguchi and A. W. Addison, *J. Chem. Soc., Dalton Trans.*, 600 (1979).
18 M. D. Timkin, D. N. Hendrickson and E. Sinn, *Inorg. Chem., 24*, 3947 (1985).
19 R. A. Palmer and T. S. Piper, *Inorg. Chem., 5*, 864 (1966).
20 W. T. Oosterhuis, *Struct. Bonding (Berlin), 20*, 59 (1974).
21 A. Ohyoshi, J. Honbo, N. Matsumoto, S. Ohta and S. Sakamoto, *Bull. Chem. Soc. Jpn., 59*, 1611 (1986).
22 K. M. Kadish, K. Das, D. Schaeper, C. L. Merrill, B. R. Welch and L. J. Wilson, *Inorg. Chem., 19*, 2816 (1980).
23 E. R. Brown and R. F. Large, in A. Weissberger and B. W. Rossiter (eds.), 'Techniques of Chemistry, Vol. I, Physical Methods of Chemistry, Part IIA Electrochemical Methods', Wiley, New York, 1971, p. 423.