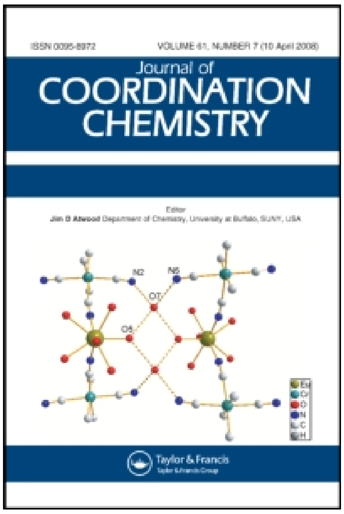

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IRON(III) COMPLEXES OF *N*-BENZOYL-*N'*-SALICYLIDENEHYDRAZINES: SYNTHESIS, CHARACTERIZATION AND PROPERTIES

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A series of iron(III) complexes of *N*-benzoyl-*N'*-salicylidenehydrazine and its substituted derivatives (H_2bhsX; X = H, OMe, Cl, NO_2) with the general molecular formula K[Fe(bhsX)$_2$] were synthesized in methanolic media by reacting anhydrous $FeCl_3$, H_2bhsX and KOH in 1:2:4 mol ratio. The complexes were characterized using analytical, magnetic, spectroscopic and electrochemical techniques. In each complex the ligand binds the metal ion meridionally *via* the phenolate-O, imine-N and amide-O atoms. Room temperature solid state magnetic moments (5.75–6.09 μ_B) of the complexes are very similar and correspond to an S = 5/2 state. EPR spectra of the complexes reveal a subtle rhombic distortion of the $Fe^{III}O_4N_2$ sphere. Ligand-to-metal charge transfer bands are observed in the visible region (585 - 400 nm) of the electronic spectra. These bands shift to lower energy as the electron donating ability of the coordinated phenolate function increases. In cyclic voltammetry the complexes display an Fe(III) → Fe(II) reduction (–0.75 to –1.12 V) and irreversible oxidations (0.96–1.39 V). The redox potentials are significantly influenced by the electronic nature of the substituents. A linear correlation between the Fe(III)-Fe(II) reduction potentials and Hammett substituent constants is observed.

Keywords: high-spin iron(III); deprotonated amide; amide-O coordination; redox

INTRODUCTION

Higher-valent first row transition metal complexes are of considerable interest because of the participation of these metal ions in several biological redox processes.[1] Deprotonated amide nitrogen is known to stabilize high oxidation states of transition metals.[2] Proton coupled electron transfer between the metal ion and the coordinated ligand involving the hydrogen attached to the carbon

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atom α to the deprotonated nitrogen atom is encountered quite often in these complexes.[3] As a result the metal ion is reduced at the expense of ligand oxidation. The commonly used approach to avoid this problem is the replacement of the *α*-hydrogen atoms by alkyl groups.[4] Another could be use of the oxygen atom of the deprotonated amide function instead of the nitrogen atom for metal coordination. Amide oxygen coordinated, higher-valent species are scarcely known. Recently, we reported the first example of such a species, a manganese(IV) complex having oxygen atoms of the deprotonated amide function in the coordination sphere.[5] The ligand used was *N*-benzoyl-*N'*-salicylidenehydrazine (H_2bhsH). We have subsequently explored the possibility of using this ligand and its substituted derivatives to obtain higher-valent iron complexes. Herein we report the syntheses, spectroscopic, magnetic and electrochemical properties of a series of mononuclear high-spin iron(III) complexes. Relationships between metal ion redox or spectroscopic properties with ligand electronic properties have been established.

EXPERIMENTAL

Materials

The chemicals and solvents used in this work were of reagent grade, available commercially, and were used without further purification.

Physical Measurements

Microanalytical data were obtained by means of a Perkin-Elmer Model 240C elemental analyzer. IR spectra were measured using KBr pellets with a Jasco 5300 FT-IR spectrophotometer. A Jasco 7800 UV/vis spectrophotometer was used to record electronic spectra. Room temperature magnetic susceptibilities were measured on a Cahn 3000 magnetic balance. Diamagnetic corrections calculated from Pascal's constants[6] were used to obtain molar paramagnetic susceptibilities. EPR spectra were measured using a JEOL FE-3X spectrometer. A Cypress model CS-1090/CS-1087 electroanalytical system was used for cyclic voltammetric experiments with dimethylformamide solutions of the complexes containing tetrabutylammonium perchlorate as supporting electrolyte. The three electrode measurements were carried out at 298 K under a dinitrogen atmosphere with a platinum disk working electrode, a platinum wire auxiliarly electrode and an Ag-AgCl reference electrode. The potentials reported in this work are uncorrected for junction contributions.

Preparation of Compounds

The ligands were prepared in high yield (80–90%) by the reaction of one equivalent of benzoylhydrazine with one equivalent of the corresponding aldehyde in methanol. All the complexes were synthesized by following similar methods. Details are therefore given for a representative case.

$K[Fe(bhsCl)_2]$

To a methanol solution (15 cm^3) of H_2bhsCl (466 mg, 1.7 mmol) and KOH (190 mg, 3.4 mmol) a 5 cm^3 methanol solution of anhydrous $FeCl_3$ (138 mg, 0.85 mmol) was added. The mixture was stirred at room temperature in air for 1 h. The complex separated as a dark brown solid, was collected by filtration, washed with methanol followed by water and finally dried in vacuum over anhydrous $CaCl_2$. Yield: 180 mg (42%). *Anal.* Calcd. for $KFeC_{28}H_{18}N_4O_4Cl_2$(%): C, 52.52; H, 2.83; N, 8.75. Found: C, 52.29; H, 3.33; N, 9.04.

Analytical data for other complexes prepared by similar procedure are as follows. *Anal.* Calcd. for $K[Fe(bhsH)_2]$, $KFeC_{28}H_{20}N_4O_4$(%): C, 58.85; H, 3.53; N, 9.81. Found: C, 59.12; H, 3.87; N, 10.13. *Anal.* Calcd. for $K[Fe(bhsOMe)_2]$, $KFeC_{30}H_{24}N_4O_6$(%): C, 57.06; H, 3.83; N, 8.87. Found: C, 57.34; H, 3.97; N, 8.95. *Anal.* Calcd. for $K[Fe(bhsNO_2)_2]$, $KFeC_{28}H_{18}N_6O_8$(%): C, 50.85; H, 2.74; N, 12.71. Found: C, 50.38; H, 3.06; N, 12.30.

RESULTS AND DISCUSSION

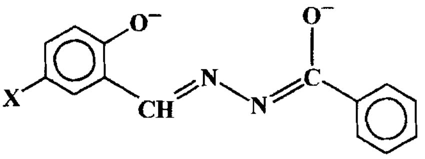
Synthesis and Properties

The complexes were synthesized from methanol by reacting one equivalent of anhydrous $FeCl_3$, two equivalents of the corresponding ligand and four equivalents of KOH. Elemental analyses are satisfactory with the general formula $K[Fe(bhsX)_2]$. Infrared spectra of the complexes do not display the free ligand O-H (~ 3300 cm^{-1}), N-H (~ 3100 cm^{-1}) and C=O (~ 1675 cm^{-1}) stretches.[7] A strong peak observed at ~1600 cm^{-1} for the complexes is assigned[8] to the conjugate C=N—N=C moiety of the coordinated ligands. Thus, in the complexes the amide function of the ligands exists in the enolate form. In each complex the ligand binds the metal ion meridionally *via* the imine-N, phenolate-O and deprotonated amide-O atoms forming a six- and a five-membered chelate ring. This type of coordination to metal ions by $bhsH^{2-}$ and similar ligands has been confirmed by solid state X-ray structure determinations.[9] The strong band observed for each complex at ~ 1550 cm^{-1}

TABLE I Magnetic Moment, EPR and Electronic Spectral Data

complex	μ_{eff}/μ_B [a]	g [b]	$\lambda_{max}/nm(\in/M^{-1}cm^{-1})$ [c,d]
$K[Fe(bhsOMe)_2]$	6.09	4.13, 5.08, 7.10	585^{sh}, 525^{sh}, 470 (7650), 405^{sh}, 385 (23300)
$K[Fe(bhsH)_2]$	5.97	4.16, 5.05, 7.30	550^{sh}, 497^{sh}, $465,^{sh}$, 440 (7450), 390^{sh}, 365 (25500) 355^{sh}
$K[Fe(bhsCl)_2]$	6.01	4.12, 5.30, 7.36	550^{sh}, 500^{sh}, 470^{sh}, 447 (6500), 392^{sh}, 372 (21500) 355^{sh}
$K[Fe(bhsNO_2)_2]$	5.75	4.16, 5.47, 7.46	535^{sh}, 485^{sh}, 455^{sh}, 383 (48000), 290 (50300)

[a] At 300 K. [b] In dimethylformamide-toluene (4:1). [c] In dimethylformamide. [d] sh, shoulder.



X = H, $bhsH^{2-}$
X = OMe, $bhsOMe^{2-}$
X = Cl, $bhsCl^{2-}$
X = NO_2, $bhsNO_2^{2-}$

is most probably due to C=C stretches.[10] The solid state magnetic susceptibility measurements (Table I) at room temperature (298 K) suggest an $S = 5/2$ spin state in each complex.

EPR Spectra

X-band EPR features of all the complexes are very similar and characteristic of an $S = 5/2$ system. A strong signal at $g \approx 4$ is observed for each of the complexes (Table I). The EPR features of a hexacoordinated high-spin d^5 system depend on the nature of distortion from octahedral symmetry.[11] In such a situation the magnetic level consists of three Kramers doublets. The ratio of the rhombic (E) and axial (D) zero-field splitting parameters ($\lambda = E/D$) and their values determine the complexity of the EPR spectrum. In a completely rhombic field ($\lambda = 1/3$) a strong signal at $g = 30/7$ is expected from the middle Kramers doublet. This signal may split or becomes broad if l deviates from 1/3. In all the complexes there are two weak absorptions at g values of ~ 5 and ~ 7. These absorptions most probably indicate[11] little deviation from complete rhombicity.

Electronic Spectra

The electronic spectra of the complexes are very similar. Data are summarized in Table I. In the visible region the complexes display a shoulder in the range 530 – 585 nm followed by a couple of shoulders and a peak in the range 440 – 470 nm. At higher energy a strong absorption at ~ 380 nm preceeded by a shoulder at ~ 400 nm is observed. Strong absorptions in the range 400–600 nm are reported[12] for Schiff base complexes of iron(III). It has been proposed[13] that the origin of these bands is the charge transfer transition from the ligand phenolate orbitals (pπ) to metal orbitals (dπ*). In the electronic spectra of high-spin iron(III) complexes the charge transfer band shows a red shift as the coordinated ligand changes from a poor electron donor to a better donor.[13,14] The present series of complexes behaves similarly. As the electron donating ability of the phenolate oxygen increases the band positions generally shift to lower energy (Table I). However, the peak positions for $K[Fe(bhsH)_2]$ and $K[Fe(bhsCl)_2]$ are almost identical. The low energy shift of the band positions is expected due to the decrease in the ligand pπ and metal dπ* energy level separation as the substituent at the *para* position of the phenolate oxygen becomes more electron donating. The intense band at ~ 380 nm does not show this trend. This band is possibly due to an intraligand transition.

Redox Properties

The complexes display a *quasi*-reversible to irreversible reduction couple at potentials negative to the Ag/AgCl electrode. The one electron stoichiometry of this redox response is established by comparing the current heights with known one electron redox processes under identical conditions. This response is assigned to the Fe(III) → Fe(II) reduction. Formal potentials for this couple are sensitive to the nature of the substituents on the *para* position of the coordinated phenolate function. $E_{1/2}$ values shift in the cathodic direction with the increase of electron donating ability of the substituents (Table II). When these potentials are plotted against the Hammett substituent constants (σ_p)[15] a linear correlation is observed (Figure 1). Thus, as the electron density on the phenolate function increases Fe(III) to Fe(II) reduction becomes more difficult. Irreversible oxidation responses are observed at potentials positive to the Ag/AgCl electrode (Table II). At present it is not clear whether any of the observed oxidation responses is metal centred or not. However, free H_2bhsCl and H_2bhsNO_2 do not display any response up to 1.5 V under identical conditions. On the other hand free H_2bhsH and $H_2bhsOMe$ display an irreversible oxidation at ~ 1.3 V with very high current. The current height of the first oxidation response in each complex is comparable with that of the Fe(III) to

TABLE II Cyclic Voltammetric Data[a, b]

complex	$E_{1/2}/V$ (ΔE_p/mV)	E_{pa}/V
$K[Fe(bhsOMe)_2]$	-1.12 (80)	0.96, 1.08, 1.17
$K[Fe(bhsH)_2]$	-1.05 (70)	1.20, 1.39
$K[Fe(bhsCl)_2]$	-0.95 (100)	1.24, 1.45
$K[Fe(bhsNO_2)_2]$	-0.75 (260)	1.39

[a] In dimethlformamide (0.1 M TBAP) at a platinum at 298 K. [b] E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential; $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_p = E_{pa} - E_{pc}$.

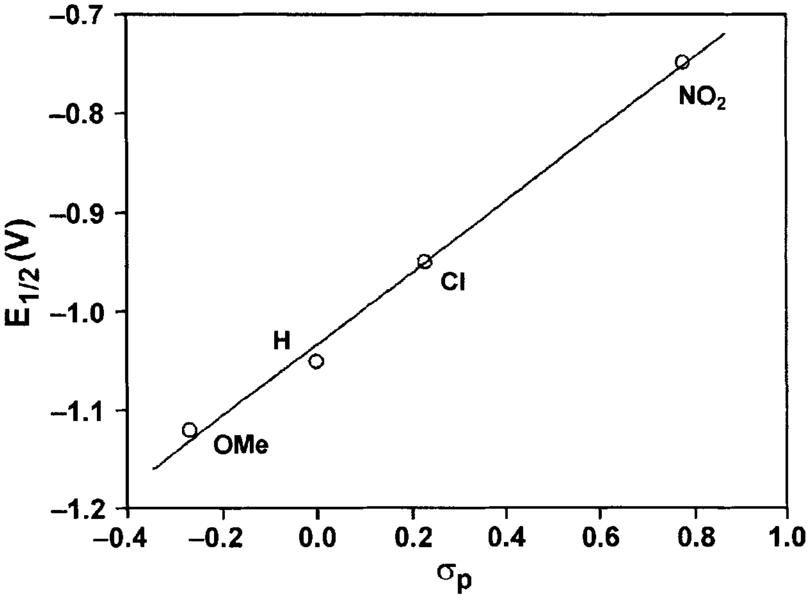


FIGURE 1 Correlation between the Fe(III)-Fe(II) reduction potentials and the Hammett substituent constants for the complexes. The straight line represents a linear, least-squares fit.

Fe(II) reduction. Therefore, we tentatively assign the first oxidation wave due to Fe(III) → Fe(IV) process. The electronic nature of the substituents affect the oxidation potentials similarly (Table II) as in the case of the Fe(III) → Fe(II) reduction.

In search of amide oxygen coordinated, higher valent iron species we have isolated and characterized *bis* complexes of high-spin iron(III) with *N*-benzoyl-*N′*-salicylidenehydrazine and its substituted derivatives. The ligands coordinate the metal ion *via* amide-O, imine-N and phenolate-O in meridional fashion. The EPR spectra of the complexes are typical for rhombic distortion of the FeO_4N_2 octahedron. The ligand-to-metal charge transfer transitions and Fe(III) → Fe(II) reductions are strongly influenced by ligand electronic properties. The complexes indeed display irreversible oxidations in cyclic voltammetry. The lowest potential oxidation response possibly involves the metal centre.

Acknowledgments

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