Oxo-bridged Complexes of Iron(III) Derived from 2-(2′-Hydroxyphenyl)-benzothiazole and 2-(2′-Hydroxyphenyl)benzimidazole Ligands

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Abstract

Iron(III) complexes containing substituted 2-(2′-oxyphenyl)benzothiazole (PBT) and 2-(2′-oxyphenyl)benzimidazole (PBI) ligands were prepared. These have mostly been characterized as oxo-bridged compounds by their magnetic susceptibility and EPR behavior with a general formula $[Fe(L)_2]_2O$. Most of the compounds have limited solubility, with the methoxy- and dimethylamino-substituted analogues being somewhat more soluble. Diffuse reflectance spectra and solution optical spectra indicate some effect of ligand basicity on the position of the phenolate to iron(III) charge-transfer band with electron-releasing substituents on the ligands shifting this band to lower energy. In the benzimidazole complex this band was shifted to higher energy relative to its benzothiazole counterpart. Electrochemical studies show irreversible electron transfer and indicate a stabilization of the iron(III) oxidation state relative to iron(II) by electron-releasing substituents on the ligand. Temperature dependent magnetic susceptibility reveals that most of the compounds are strongly antiferromagnetically coupled.

Introduction

The structure and magnetic properties of oxo-bridged compounds are of considerable interest since they can act as models for oxygen binding in biological systems [1–4]. Oxo-bridged binuclear iron occurs in the invertebrate oxygen transport protein hemerythrin, in ribonucleotide reductase of *Escherichia coli*, in reduced component A of methane monooxygenase from *Methylococcus capsulatus*, and in purple acid phosphatases from beef spleen and pig allantoic fluid [5, 6]. Iron(III) complexes possessing bridging oxide have been subjected to variable temperature magnetic susceptibility [7, 8], electron spin resonance and Mössbauer studies [9–11], and X-ray structural determinations [12]. This class of compounds is reported to display substantial antiferromagnetism which has been attributed to superexchange coupling of $S = \frac{5}{2}$ ferric ions via the oxo bridge.

Recent X-ray crystallographic studies [9] have revealed quite a marked variation in the Fe–O–Fe bridging angle, which may be affected by variation in electronic and steric factors. Magnetic data has indicated that the magnitude and sign of the coupling constants are principally determined by the geometry of the bridging unit and the electron density at the oxygen bridge [12, 13]. However the effect of the Fe–O–Fe bridging angle on the degree of coupling is not yet completely understood.

The compounds studied in this paper further have the characteristic of containing phenolate donor ligands and can thus serve as models for iron-tyrosinate proteins [14, 15]. Among these are the transferrins, the catechol dioxygenases and the purple acid phosphatases. We have attempted to investigate the effect of the ligand composition on the position of the phenolate-to-iron(III) charge-transfer bands and compare this to previous work in this area [16–18]. The ligands used in this study are shown in Fig. 1.

Experimental

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 three-electrode cell configuration was controlled with

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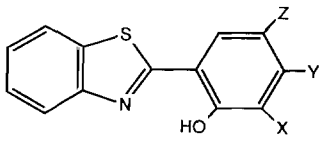
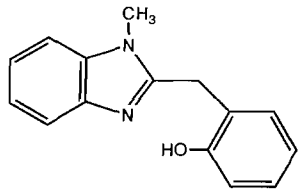


PBTH	X= H, Y= H, Z= H
3-MePBTH	X= CH_3, Y= H, Z= H
5-MePBTH	X= H, Y= H, Z= CH_3
3-MeOPBTH	X= OCH_3, Y= H, Z= H
5-MeOPBTH	X= H, Y= H, Z= OCH_3
3,4-MeOPBTH	X= OCH_3, Y= OCH_3, Z= H
4-NMePBTH	X= H, Y= $N(CH_3)_2$, Z= H



BzMeBIH

Fig. 1. Ligands used in this study.

a system comprising a PAR-173 potentiostat, a PAR-176 i/E converter and a PAR-175 waveform generator. Potentials in non-aqueous solution 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 +300 mV versus a saturated calomel electrode in acetonitrile [19]. The potentials may thus be approximated with reference to the SHE by the addition of *c.* 545 mV. A Beckman rotating platinum disc electrode (area 0.300 cm^2) or a rotating mercury/gold amalgam disc electrode were used for rotating disc polarography (r.d.p.) and also as a stationary planar electrode for cyclic voltammetry.

Nuclear magnetic resonance spectra were obtained at ambient temperature on a JEOL FX90Q (90 MHz) FT instrument, chemical shifts being quoted with respect to tetramethylsilane as internal standard. The NMR spectra are reported as: δ value (multiplicity, integral, coupling constant, assignment). Optical spectra are reported as: wavelength in nm (molar absorptivity in dm^3 mol^{-1} cm^{-1}). Mass spectra were recorded on a Finnigan-4000 GC-MS, with the data for the lower mass fragments truncated below *m/e* = 46 and 5% intensity. Solution optical spectra were obtained using a Perkin-Elmer Lambda-3B spectrophotometer and diffuse reflectance spectra of solids on a PE-330 equipped with an integrating sphere. Magnetic susceptibility measurements for $[Fe(PBT)_2]_2O$ and $[Fe(3\text{-}MePBT)_2]_2O$, were carried out in the range 10 to 320 K using a cryostat-controlled SQUID magnetometer (Charlottesville). The calibration and method of calibration were as described previously [20]. Magnetic susceptibility measurements for $[Fe(5\text{-}MePBT)_2]_2O$, $[Fe(3\text{-}MeOPBT)_2]_2O$, $[Fe(5\text{-}MeOPBT)_2]_2O$, $[Fe(3,4\text{-}MeOPBT)_2]_2O$, $[Fe(4\text{-}NMe_2PBT)_2]_2O$ and $[Fe(PMeBI)_2]_2O$ were obtained by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance (St. Johns). A main solenoid field of 1.5 T and a gradient field of 10 T m^{-1} were employed. Diamagnetic corrections were applied using Pascal's constants when the ligand diamagnetism was not measured directly [21]. Melting points are uncorrected. Microanalyses (C, H, N, S) were performed by Canadian Microanalytical Service Ltd. (Vancouver) and (Fe) Galbraith Laboratories (Knoxville). Reagents were used for syntheses as received from Sigma, Aldrich, Fisher (anhydrous iron(III) chloride) and G. F. Smith (iron(III) perchlorate·$9H_2O$).

2-(2'-Hydroxy-3'-methylphenyl)benzothiazole (3-MePBTH)

This was prepared by stirring 3-methylsalicylic acid (11.42 g, 75 mmol) and 2-aminothiophenol (9.40 g, 75 mmol) in 200 g of polyphosphoric acid for two hours at 220 °C. The hot mixture was poured slowly into 1 l of vigorously stirred cold water. Solid sodium hydroxide was added to make the solution strongly basic and the solution was heated to 90 °C and stirred for 2 h. The pH of the solution was then adjusted to 7 with concentrated sulfuric acid, resulting in the formation of a white solid. The slurry was cooled and the product filtered off. Recrystallization from ethanol and drying *in vacuo* (P_4O_{10}) gave 14.2 g (68% yield) of white needles, melting point (m.p.) 129 °C. MS: (*m/e*) 243(6%), 242(18%), 241(M^+, 100%), 240(16%), 213(10%), 212(53%), 121(9%), 109(21%), 108(9%), 77(9%), 69(14%), 65(10%), 63(9%), 51(9%), 40(13%). NMR ($CDCl_3$): 2.36 (s, 3, CH_3), 6.85 (t, 1, arom.), 7.21 (s, 1, OH), 7.45 (m, 3, arom.), 7.90 (t, 2, arom.). UV (methanol): 333 (15 500), 303 (sh, 14 000), 290 (16 200), 282 (sh, 14 000), 238 (6500), 230 (6000). *Anal.* Calc. for $C_{14}H_{11}NOS$: C, 69.7; H, 4.59; N, 5.81. Found: C, 68.9; H, 4.55; N, 5.74%.

2-(2'-Hydroxy-5'-methylphenyl)benzothiazole (5-MePBTH)

This was prepared by combining 5-methylsalicylic acid (5.7 g, 37.5 mmol) and 2-aminothiophenol (4.7 g, 37.5 mmol) in 100 g of polyphosphoric acid and stirring the mixture for 2 h at 200 °C. The procedure used for workup was the same as for the previous compound. Recrystallization from ethanol (charcoal) and drying *in vacuo* (P_4O_{10}) gave 2.4 g (28% yield) of white solid, m.p. 127 °C. MS: (*m/e*) 243(6%), 242(17%), 241(M^+, 100%), 240(31%), 213(8%), 212(38%), 121(13%), 109(35%), 108(10%), 107(7%), 106(7%), 105(7%), 93(7%), 78(7%), 77(16%), 69(30%), 65(24%), 63(19%), 58(7%),

52(10%), 51(19%), 50(7%). NMR ($CDCl_3$): 2.33 (s, 3, CH_3), 6.03 (t, 2, arom.), 7.23 (s, 1, OH), 7.45 (m, 3, arom.), 7.91 (t, 2, arom.). UV (methanol): 340 (14 900), 302 (sh, 12 000), 290 (15 300), 280 (sh, 13 600), 258 (7200), 250 (sh, 7400). *Anal.* Calc. for $C_{14}H_{11}NOS$: C, 69.7; H, 4.59; N, 5.81. Found: C, 69.5; H, 4.63; N, 5.84%.

2-(2'-Hydroxyphenyl)benzothiazole (PBTH)

This was used as received from Aldrich Chemical Company. UV (methanol): 332 (13 000), 298 (9000), 286 (11 000), 256 (6000), 248 (6000).

2-(2'-Hydroxy-3'-methoxyphenyl)benzothiazole (3-MeOPBTH)

This was prepared by combining 3-methoxysalicylic acid (12.6 g, 75 mmol) and 2-aminothiophenol (9.4 g, 75 mmol) in 100 g of polyphosphoric acid and stirring the mixture for two hours at 210 °C. The same procedure was used for workup as before. Recrystallization from methanol (charcoal) and drying *in vacuo* (P_4O_{10}) gave a pale green solid, m.p. 157 °C. MS: (*m/e*) 258(19%), 257(M^+, 100%), 246(45%), 239(36%), 228(33%), 227(16%), 214(69%), 211(17%), 199(15%), 186(31%), 160(15%), 136(24%), 109(30%), 108(16%), 93(24%), 80(23%), 69(40%), 65(28%), 63(25%). NMR ($CDCl_3$): 3.99 (s, 3, OCH_3), 6.94 (m, 2, arom.), 7.30 (s, 1, OH), 7.42 (m, 3, arom.), 7.98 (m, 2, arom.). UV (methanol): 335 (8200), 317 (sh, 14 000), 306 (15 000), 295 (sh, 15 000), 282 (sh, 12 000), 255 (6200), 223 (11 000). *Anal.* Calc. for $C_{14}H_{11}NO_2S$: C, 65.4; H, 4.28; N, 5.45. Found: C, 65.2; H, 4.28; N, 5.38%.

2-(2'-Hydroxy-5'-methoxyphenyl)benzothiazole (5-MeOPBTH)

This was prepared by combining 5-methoxysalicylic acid (3.24 g, 12.6 mmol) and 2-aminothiophenol (1.58 g, 12.6 mmol) in 70 g of polyphosphoric acid and stirring for 20 h at 110 °C. Workup with strong base as before gave a brown, heterogeneous solid which was recrystallized from methanol–water and then dried *in vacuo* (P_4O_{10}) to give 0.60 g of light brown solid (19%), m.p. 157 °C. MS: (*m/e*) 257(M^+, 32%), 242(59%), 186(26%), 160(23%), 129(20%), 116(17%), 109(61%), 108(27%), 93(17%), 82(33%), 80(22%), 79(26%), 77(17%), 69(100%), 65(92%), 64(18%), 63(65%), 62(18%), 58(22%), 55(18%), 54(28%), 53(31%), 52(31%), 51(55%), 50(23%). NMR ($CDCl_3$): 3.84 (s, 3, OCH_3), 7.03 (s, 2, arom.), 7.14 (s, 1, OH), 7.45 (m, 3, arom.), 7.92 (m, 2, arom.). UV (methanol): 355 (1200), 310 (sh, 11 000), 292 (16 000), 284 (sh, 15 000), 257 (sh, 8000), 250 (sh, 9000). *Anal.* Calc. for $C_{14}H_{11}NO_2S$: C, 65.4; H, 4.28; N, 5.45. Found: C, 65.0; H, 4.36; N, 5.41%.

2-(2'-Hydroxy-3'-4'-dimethoxyphenyl)benzothiazole (3,4-MeOPBTH)

This was prepared by combining 3,4-dimethoxysalicylic acid (3.0 g, 17 mmol) and 2-aminothiophenol (6.25 g, 50 mmol) in 50 g of polyphosphoric acid and stirring the mixture for 1 h at 120 °C. The hot mixture was then poured slowly into 500 ml of hot, strongly basic potassium hydroxide solution and the solution stirred for 2 h at 90 °C. Concentrated hydrochloric acid was used to adjust the pH to 7 before cooling the solution and filtering off the solid. Recrystallization from ethanol (charcoal) and drying *in vacuo* (P_4O_{10}) gave 1.40 g (30%) of light purple crystals, m.p. 182 °C. MS: (*m/e*) 287(M^+, 64%), 272(33%), 269(50%), 244(42%), 241(25%), 201(41%), 173(70%), 172(15%), 136(17%), 122(15%), 109(19%), 108(15%), 93(18%), 86(100%), 69(44%), 65(27%), 63(24%), 51(15%). NMR ($CDCl_3$): 3.91 (s, 3, OCH_3), 3.97 (s, 3, OCH_3), 6.52 (d, 1, arom.), 7.26 (s, 1, OH), 7.44 (m, 3, arom.), 7.88 (m, 2, arom.). UV (methanol): 345 (sh, 18 700), 330 (24 600), 307 (sh, 17 400), 295 (sh, 14 800), 295 (sh, 14 800), 243 (sh, 13 600), 220 (31 200), 203 (sh, 22 000). *Anal.* Calc. for $C_{15}H_{13}NO_3S$: C, 62.7; H, 4.56; N, 4.87. Found: C, 62.7; H, 4.56; N, 4.88%.

2-(2'-Hydroxy-4'-dimethylamino)benzothiazole (4-Me_2NPBTH)

This was prepared by combining 4-dimethylaminosalicylic acid (6.80 g, 37.5 mmol) and 2-aminothiophenol (5.22 g, 37.5 mmol) in 50 g of polyphosphoric acid and stirring the mixture for 2 h at 210 °C. (Initially there was significant effervescence due to partial decarboxylation of the acid.) The product was worked up as described before. Recrystallization from methanol and then acetonitrile (charcoal), followed by drying *in vacuo* (P_4O_{10}) gave 1.1 g (11%) of pale yellow solid, m.p. 217 °C. MS: (*m/e*) 271(20%), 270(M^+, 100%), 269(31%), 255(16%), 227(15%), 199(19%), 198(22%), 160(10%), 122(10%), 121(61%), 113(118%), 109(21%), 108(14%), 92(10%), 82(15%), 77(10%), 69(34%), 65(28%), 64(10%), 63(33%), 51(13%). NMR ($CDCl_3$): 3.02 (s, 6, CH_3), 6.29 (m, 2, arom.), 7.42 (m, 3, arom.), 7.82 (m, 2, arom.). UV (methanol): 375 (43 000), 365 (sh, 41 000), 308 (5400), 297 (4700), 258 (12 000), 222 (25 000), 204 (27 000). *Anal.* Calc. for $C_{15}H_{13}N_2OS$: C, 66.7; H, 5.19; N, 10.4. Found: C, 66.9; H, 5.26; N, 10.4%.

2-(2'-Hydroxyphenyl)benzimidazole (PBIH)

This was made as previously described [22].

2-(2'-Hydroxybenzyl)-N-methylbenzimidazole (BzMeBIH)

2-Hydroxyphenylacetic acid (6.08 g, 40 mmol) and *N*-methyl-*o*-phenylenediamine dihydrochloride (7.80 g, 40 mmol) were refluxed in 4 M hydrochloric

acid (50 ml) for 75 h. Cooling gave a light blue crystalline solid which was dissolved in ethanol and the pH adjusted to 7 with 5 M NaOH. The volume of solvent was reduced (rotary evaporation) to a few ml and 100 ml of water added. The resulting grey solid was filtered off, recrystallized from ethanol (charcoal) and dried *in vacuo* (P_4O_{10}) to give 6.6 g (70% yield) of pink solid, m.p. 123–126 °C. MS: (*m/e*) 239(9%), 238(M^+, 46%), 237(8%), 222(8%), 221(41%), 133(12%), 132(100%), 136(17%), 131(38%), 119(12%), 107(20%), 105(11%), 104-(20%), 103(11%), 92(14%), 91(16%), 78(19%), 77(55%), 65(15%), 63(15%). NMR ($CDCl_3$): 3.80 (s, 3, NCH_3), 4.47 (s, 2, CH_2), 4.91 (s, 1, OH), 6.70 (t, 1, arom.), 7.01 (t, 1, arom.), 7.15 (m, 1, arom.), 7.39 (m, 4, arom.), 7.74 (m, 1, arom.). UV (ethanol): 283 (8200), 276 (9000), 269 (sh, 7200), 254 (7200), 248 (sh, 6800), 228 (sh, 2100). *Anal.* Calc. for $C_{15}H_{14}N_2O$: C, 75.6; H, 5.92; N, 11.76. Found: C, 75.5; H, 5.86; N, 11.7%.

Attempts to prepare a nitro-substituted 2-(2′-hydroxyphenyl)benzothiazole from 5-nitrosalicylic acid and 2-aminothiophenol were unsuccessful.

$Fe(PBT)_2Cl$

A hot solution of anhydrous $FeCl_3$ (0.81 g (5 mmol) in 50 ml absolute ethanol was added to a solution of 2-(2′-hydroxyphenyl)benzothiazole (1.15 g, 5 mmol) in 100 ml of hot absolute ethanol. After 48 h the brown solution was rotary evaporated to about one-third of the original volume and then stored at −8 °C for four days. Filtering and washing resulted in a small amount of dark brown solid and some unreacted ligand. The dark solid was separated manually and dried *in vacuo* at 153 °C to give 0.20 g (7.4% yield). After 5 days the mother liquor was refiltered and this resulted in 0.35 g of a fine red–brown solid which was dried *in vacuo* (P_4O_{10}) and gave the same elemental analysis as the original product. Total yield 0.55 g (29%). *Anal.* Calc. for $C_{26}H_{16}ClFeN_2O_2S_2$: C, 57.4; H, 2.97; N, 5.15; Fe, 10.27. Found: C, 57.3; H, 2.93; N, 5.14; Fe, 10.31%.

$[Fe(PBT)_2]_2O$

A DMF solution (20 ml) of 2-(2′-hydroxyphenyl) benzothiazole (2.04 g, 9 mmol) was added to a like solution of iron(III) perchlorate·$9H_2O$ (1.06 g, 2 mmol) and then 0.91 g (9 mmol) of triethylamine was added. The red–brown precipitate was filtered off, washed with ethanol, and dried *in vacuo* (P_4O_{10}) to give 1.06 g (34% yield). *Anal.* Calc. for $C_{52}H_{32}Fe_2N_4O_5S_4$: C, 60.5; H, 3.12; N, 5.42; Fe, 10.8. Found: C, 60.9; H, 2.62; N, 5.51; Fe, 10.8%.

$[Fe(3\text{-}MePBT)_2]_2O$

To a solution of 3-MePBTH (2.41 g, 10 mmol), triethylamine (1.22 g, 12 mmol) and 2 ml of triethyl orthoformate in 50 ml of DMF was added a solution of iron(III) perchlorate·$9H_2O$ (1.42 g, 2.75 mmol) and 2 ml of triethyl orthoformate in 20 ml of DMF. After 24 h the resulting dark brown crystals were filtered off and dried *in vacuo* (P_4O_{10}). *Anal.* Calc. for $C_{56}H_{40}Fe_2N_4O_5S_4$: C, 61.8; H, 3.70; N, 5.15; Fe, 10.16. Found: C, 61.3; H, 3.76; N, 5.49; Fe, 9.80%.

$[Fe(5\text{-}MePBT)_2]_2O\cdot\frac{1}{2}DMF$

To a warm solution of 5-MePBTH (0.45 g, 1.9 mmol) and triethylamine (0.19 g, 1.9 mmol) in 20 ml of DMF was added a solution of iron(III) perchlorate·$9H_2O$ (0.35 g, 0.68 mmol) in 20 ml of DMF followed by brief refluxing. Filtration yielded brown crystals which were washed (DMF) and dried *in vacuo* at 153 °C to give 0.30 g (43% yield). *Anal.* Calc. for $C_{56}H_{40}Fe_2N_4O_5S_4\cdot\frac{1}{2}C_3H_7NO$: C, 61.8; H, 3.90; N, 5.60; Fe, 9.92. Found: C, 61.4; H, 3.82; N, 5.44; Fe, 9.53%.

$[Fe(3\text{-}MeOPBT)_2]_2O\cdot CH_3CN\cdot H_2O$

To a solution of 3-MeOPBTH (0.39 g, 1.5 mmol) and triethylamine (0.15 g, 1.5 mmol) in 30 ml of acetone was added solid iron(III) perchlorate·$9H_2O$ (0.28 g, 0.5 mmol). The mixture was refluxed for one hour, cooled and filtered. The resulting solid was recrystallized from acetonitrile and dried *in vacuo* at 153 °C to give a black crystalline product. *Anal.* Calc. for $C_{56}H_{40}Fe_2N_4O_9S_4\cdot CH_3CN\cdot H_2O$: C, 57.5; H, 3.74; N, 5.78; Fe, 9.22. Found: C, 57.6; H, 4.47; N, 5.84; Fe, 9.25%.

$[Fe(3\text{-}MeOPBT)_2]_2O\cdot 3H_2O$

To a hot solution of 3-MeOPBTH (1.42 g, 6 mmol) in 50 ml of deoxygenated (bubbling N_2) acetone was added a similarly deoxygenated solution of iron(III) perchlorate·$9H_2O$ (1.04 g, 2 mmol) in 20 ml of the same solvent. To the dark blue–green solution was added 5 ml of 2,2-dimethoxypropane and triethylamine (0.60 g, 6 mmol) resulting in immediate formation of a dark brown solid. After brief refluxing the solvent volume was reduced (rotary evaporation) under N_2 and cooled to −15 °C. Filtering, washing (acetone) gave a black powder which was dried *in vacuo* at 153 °C to give 0.36 g (30% yield). *Anal.* Calc. for $C_{56}H_{40}Fe_2N_4O_9S_4\cdot 3H_2O$: C, 55.7; H, 3.84; N, 4.64. Found: C, 55.6; H, 3.71; N, 4.44%.

$[Fe(5\text{-}MeOPBT)_2]_2O\cdot\frac{1}{2}H_2O$

To a hot solution of 5-MeOPBTH (0.77 g, 3 mmol) in 50 ml of acetone was added a solution of iron(III) perchlorate·$9H_2O$ (0.52 g, 1 mmol) in 30 ml of the same solvent resulting in a dark green solution. Addition of 3 ml of trimethyl orthoformate and triethylamine (0.30 g, 3 mmol) was followed by a brief reflux. Subsequent addition of 100 ml of ethyl ether induced precipitation of a black powder which was filtered off, washed (acetone) and dried *in vacuo* at 150 °C to give 0.45 g (39%). *Anal.* Calc. for $C_{56}H_{40}Fe_2N_4O_9S_4\cdot\frac{1}{2}H_2O$: C, 57.9; H, 3.56; N, 4.82; Fe, 9.61. Found: C, 57.6; H, 3.48; N, 4.84; Fe, 9.42%.

[Fe(3,4-MeOPBT)$_2$]$_2$O

To a solution of 3,4-MeOPBTH (0.22 g, 0.75 mmol) in 30 ml of hot methanol was added 0.75 mmol of 1.0 M NaOH and a hot solution of anhydrous iron(III) bromide (0.074 g, 0.25 mmol) in 20 ml of methanol. After three days the solution was filtered to give a pale red–brown, crystalline solid containing a small amount of black impurity which was separated mechanically. Drying *in vacuo* (P_4O_{10}) gave 0.16 g (50% yield). *Anal.* Calc. for $C_{60}H_{48}Fe_2N_4O_{13}S_4$: C, 56.6; H, 3.80; N, 4.40. Found: C, 56.7; H, 3.79; N, 4.39%.

[Fe(3,4-MeOPBT)$_2$]$_2$O·2H$_2$O

An identical preparation to that above gave 0.10 g (20% yield) of a fine brown product. *Anal.* Calc. for $C_{60}H_{48}Fe_2N_4O_{13}S_4 \cdot 2H_2O$: C, 56.6; H, 3.80; N, 4.40; Fe, 8.53. Found: C, 56.7; H, 3.79; N, 4.39; Fe, 7.93%.

[Fe(4-Me$_2$NPBT)$_2$]$_2$O·$\frac{1}{2}$CH$_3$OH

To a solution of 4-Me$_2$NPBTH (0.405 g, 1.5 mmol) in 50 ml of methanol and 10 ml of 2-methoxyethanol was added triethylamine (0.15 g, 1.5 mmol) and solid iron(III) perchlorate·9H$_2$O (0.275 g, 0.5 mmol). The resulting solution was heated for 2 h at 100 °C (steam bath) and the solvent (rotary) evaporated to one-third the original volume. Subsequent filtration and washing (methanol) yielded a brown solid which was dried *in vacuo* at 124 °C. *Anal.* Calc. for $C_{60}H_{52}Fe_2N_8O_5S_4 \cdot \frac{1}{2}CH_3OH$: C, 59.5; H, 4.46; N, 9.18. Found: C, 59.6; H, 4.18; N, 9.14%.

[Fe(4-Me$_2$NPBT)$_2$]$_2$O·3H$_2$O

To a solution of 4-Me$_2$NPBTH (0.538 g, 2 mmol) in 50 ml of 2-methoxyethanol was added a solution of iron(III) perchlorate·9H$_2$O (0.52 g, 1 mmol) in 20 ml of the same solvent and the dark brown solution refluxed for one hour. Cooling and filtering resulted in a dark brown/black solid which was washed (2-methoxyethanol) and dried *in vacuo* at 154 °C to give 0.38 g (30% yield). *Anal.* Calc. for $C_{60}H_{52}Fe_2N_8O_5S_4 \cdot 3H_2O$: C, 57.2; H, 4.64; N, 8.90; Fe, 8.87. Found: C, 57.6; H, 4.46; N, 8.52; Fe, 8.23%.

[Fe(PBI)$_2$]$_2$O

To a hot solution of PBIH (0.209 g, 1.0 mmol) and triethylamine (0.101 g, 1 mmol) in 50 ml of absolute ethanol was added a solution of iron(III) perchlorate·9H$_2$O (0.275 g, 0.5 mmol) in 5 ml of triethyl orthoformate. The solution was refluxed for 24 h and then (rotary) evaporated to one-third the original volume, producing a red–brown solid which was filtered off and dried *in vacuo* at 124 °C. *Anal.* Calc. for $C_{52}H_{36}Fe_2N_8O_5$: C, 64.8; H, 3.76; N, 11.6. Found: C, 64.8; H, 3.67; N, 11.4%.

[Fe(PMeBI)$_2$]$_2$(OH)$_2$·1$\frac{1}{2}$H$_2$O

To a hot solution of PMeBIH (0.78 g, 3.3 mmol) in 50 ml of 2-methoxyethanol was added a hot solution of iron(III) perchlorate·9H$_2$O (0.53 g, 1.2 mmol) in 20 ml of the same solvent. The solvent was (rotary) evaporated to one-fourth the original volume, cooled and filtered to give a brown precipitate which was dried *in vacuo* at 124 °C yielding 0.45 g (27%). *Anal.* Calc. for $C_{60}H_{54}Fe_2N_8O_6 \cdot 1\frac{1}{2}H_2O$: C, 64.2; H, 5.12; N, 9.99; Fe, 10.0. Found: C, 64.3; H, 5.39; N, 9.80; Fe, 9.6%.

Repeated trials using several different crystallization techniques and different solvents yielded no crystals of suitable size or composition for X-ray diffraction.

It should also be noted that attempts to prepare mononuclear complexes using a 3:1 molar ratio of ligand to iron and careful exclusion of water produced only binuclear compounds and free ligand. The PBT and methyl-substituted PBT complexes seem to be particularly resistant to FeL_3 formation, perhaps because the limited solubility of the dimer results in precipitation of this species before the desired product can be isolated.

Results and Discussion

The ligands are bifunctional, having both a heterocyclic nitrogen donor mimetic of histidine imidazole and a tyrosine-analogous phenol. They are utilized here in their anionic forms, generated via deprotonation of the phenolic oxygen. Their syntheses rely on the methodologies [23, 24] developed for the condensation reaction of a carboxylic acid with an *o*-aminothiophenol or an *o*-phenylenediamine.

Even by using relatively anhydrous non-aqueous solvents, and triethylamine as a base, we found that iron(III) persistently forms oxo-bridged complexes with most of these ligands. The rust-brown color common to the majority of these compounds is quite typical of oxo-bridged iron(III) species. The compounds, generally of the type $[(FeL_2)_2]O \cdot x$ solvent, are for the most part only meagerly soluble in common organic solvents.

Magnetism

Magnetic susceptibility experiments are summarized in Table 1. The [Fe(PBT)$_2$]$_2$O and [Fe(3-MePBT)$_2$]$_2$O complexes showed a gradual increase in magnetic moment from 0.6 to 2.1 BM per iron in the temperature range 10–320 K. Figure 2 is a typical χ_M versus T plot. The [Fe(5-MePBT)$_2$]$_2$O compound shows a gradual increase in moment from 0.2 to 1.8 BM in the temperature range 5.0–300 K. The [Fe(3-MeOPBT)$_2$]$_2$O complex has a much higher moment

TABLE 1. Parameters for magnetic susceptibility data

Compound	J (cm^{-1})	$10^2 \times p$	$10^6 \times TIP$	θ (K)	$10^2 \times R$ [a]	$10^6 \times \chi_{diam}$ [b]
$[Fe(PBT)_2]_2O$	−114	2.20	500	0.00	0.64	450
$[Fe(3\text{-}MePBT)_2]_2O$	−103	1.75	100	−2.20	0.72	550
$[Fe(5\text{-}MePBT)_2]_2O\cdot\frac{1}{2}DMF$	−110	0.18	100	−2.60	1.06	612
$[Fe(3\text{-}MeOPBT)_2]_2(OH)_2\cdot 2H_2O$	−29	45.5	100	−3.60	0.71	626
$[Fe(5\text{-}MeOPBT)_2]_2O\cdot\frac{1}{2}H_2O$	−129	5.27	700	−3.00	1.10	594
$[Fe(4\text{-}NMe_2PBT)_2]_2O\cdot 3H_2O$	−98	22.7	100	−4.60	0.52	688
$[Fe(3,4\text{-}MeOPBT)_2]_2O\cdot 2H_2O$	−93	20.6	200	−3.20	0.97	700
$[Fe(PMeBI)_2]_2(OH)_2\cdot 1\frac{1}{2}H_2O$	−3	0.23	100	0.00	4.26	638

[a] $R = \sqrt{(\Sigma\chi^2/\Sigma(\chi - \chi_{calc})^2)}$. [b] Molar diamagnetic correction (cgsu).

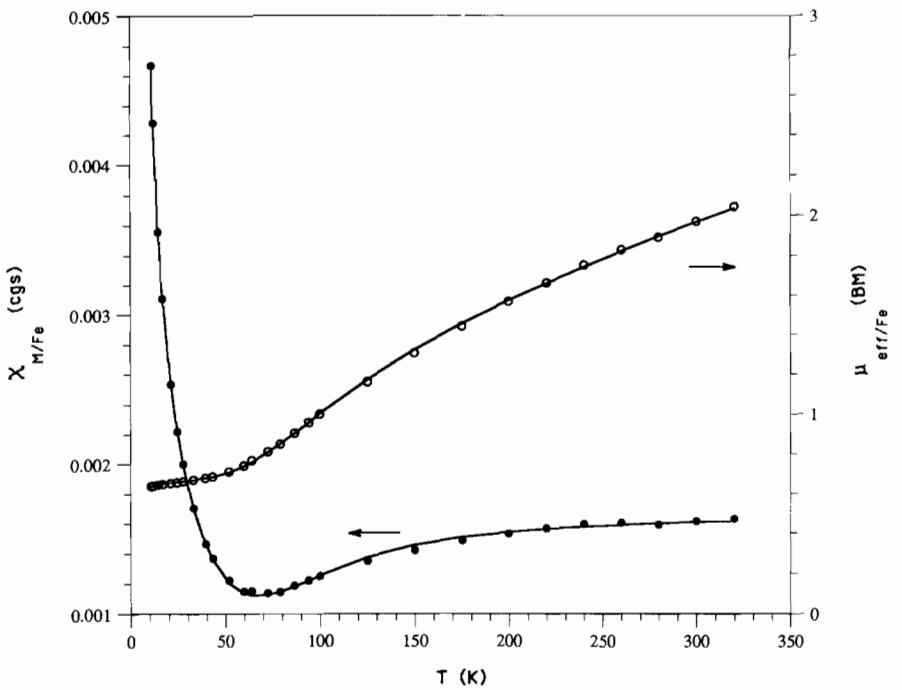


Fig. 2. Temperature dependence of magnetic susceptibility (solid circles) and effective magnetic moments (open circles) for $[Fe(PBT)_2]_2O$. The solid lines are theoretical fits using the parameters in Table 1.

(between 3.1 and 4.6 over the same temperature range) reflecting the almost 50% monomeric iron(III) content indicated by the χ_M versus temperature analysis outlined below. (This product was the result of attempting to prepare a monomeric complex through careful exclusion of water.)

$[Fe(5\text{-}MeOPBT)_2]_2O$ is similar to the first three compounds discussed above in its magnetic behavior, with a moment which gradually increases from 1.1 to 2.4 BM between 5.0 and 300 K. For $[Fe(3,4\text{-}MeOPBT)_2]_2O$ the moment varies from 2.1 to 3.3 BM reflecting the greater percentage of monomeric iron(III) present. The behavior of $[Fe(4\text{-}Me_2NPBT)_2]_2O$ is almost the same as the previous compound again showing the contribution of approximately 20% paramagnetic material.

An interesting observation is that the moment of the compounds containing methoxy and dimethylamino substituents on the ligands increases somewhat more sharply below 50 K than does the moment of the methyl substituted and unsubstituted PBT complexes.

The greatest change in moment is seen for $[Fe(PMeBI)_2]_2(OH)_2$ with a variation from 1.4 to 4.9 BM. This is consistent with the weaker coupling in this compound which allows a thermally induced population of the higher electronic energy levels at lower temperatures. Figure 3 shows the magnetic

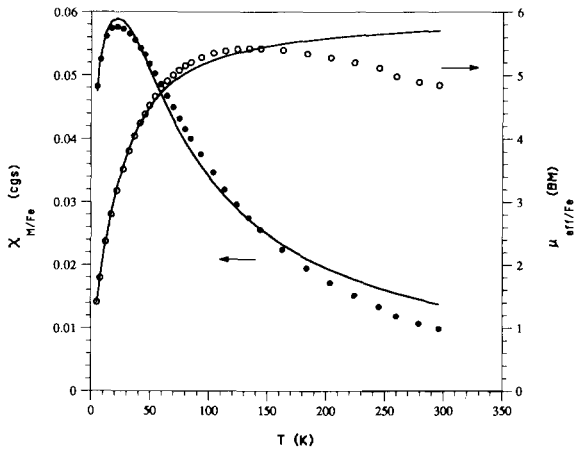


Fig. 3. Temperature dependence of magnetic susceptibility (solid circles) and effective magnetic moments (open circles) for $[Fe(PMeBI)_2]_2(OH)_2 \cdot 1\frac{1}{2}H_2O$. The solid lines are theoretical fits using the parameters in Table 1.

behavior of this compound. The magnetic susceptibility behavior of all of the compounds except $[Fe(PMeBI)_2]_2(OH)_2$ and the 3-MeOPBT complex is consistent with the presence of oxo-bridged binuclear iron(III).

Using an expression for χ_M based on the exchange Hamiltonian $\mathcal{H} = -JS_1S_2$ with $S_1 = S_2 = \frac{5}{2}$ and adding a term to correct for the fraction of monomeric high spin iron(III) impurity (p) gives the relationship

$$\chi_M = \frac{g^2\beta^2 N}{3kT} \times \left[\sum_{S=0}^{5} \frac{2(S+1)S(S+1)\exp[-JS(S+1)/2kT]}{(2S+1)\exp[-JS(S+1)/2kT]} \right] \times (1-p) + \left[\frac{35\beta^2 N}{3k(T-\theta)} \right] p + TIP$$

where N, g, β, k and T have their usual meanings, J is the magnetic exchange coupling constant, TIP is the temperature independent paramagnetism, and θ is the Weiss constant for the paramagnetic portion of the samples which is clearly evident at low temperatures [13]. For high spin iron(III) the ground state is ^6S and this is well-isolated from the lowest lying excited states. Thus g should be very close to the free-ion value of 2.0023 and this is the value used in the χ_M expression.

For a binuclear compound a given energy level has a multiplicity of $4S + 1$ and an energy $J[2S(2S + 1)]$ above that of the ground state [25]. In the case of binuclear iron(III), the $S = \frac{1}{2}$ state is $2J$ above the $S = 0$ level, which with $J = -100$ translates to an energy gap of 200 cm^{-1}.

A least-squares program was used to fit the experimental data to this equation. Most of the J values are in the range commonly observed for antiferromagnetic coupling of oxo-bridged Fe(III) dimers (−80 to −105 cm^{-1}) [12, 26]. The higher value of J for the $[Fe(5\text{-MeOPBT})_2]_2O$ complex is most likely due to structural features and not electronic factors. There is no trend toward higher or lower J as the electron donating methyl, methoxy and dimethylamino groups are added to the ligands.

The magnetism of $[Fe(PMeBI)_2]_2(OH)_2$ indicates only slight antiferromagnetic coupling with $J = -3$ cm^{-1}. This low value of J is the principal reason for assigning this compound a bis μ-hydroxo structure. It is likely that the 3-MeOPBT complex is similarly bridged. There are numerous examples of reduced antiferromagnetic coupling with $J \approx -10$ cm^{-1} with this type of bridging between the two iron atoms [27, 28]. One of the best characterized is $[Fe(Picolinate)_2]_2(HO)_2$ with $J = -8$ cm^{-1} [29]. As noted above, much more negative values of J are typically observed for oxo-bridged complexes.

Electron Spin Resonance

The complex $[Fe(PBT)_2]_2O$ gave a complicated ESR spectrum (Fig. 4) of the type previously observed for salicylideniminatoiron(III) oxo-bridged

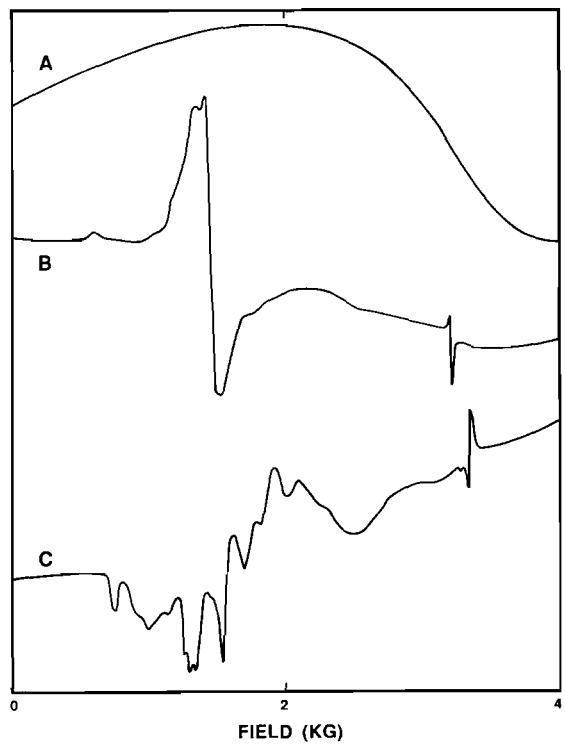


Fig. 4. ESR spectra for three of the compounds studied: (A) $[Fe(PMeBI)_2]_2(OH)_2 \cdot 1\frac{1}{2}H_2O$, (B) $Fe(PBT)_2Cl$, (C) $[Fe(PBT)_2]_2O$. 1 $G = 10^{-4}$ T.

TABLE 2. Electron spin resonance data

Compound	State, T (K)	g factors						
$Fe(PBT)_2Cl$	solid, 300						1.99[a]	
	solid, 77	9.46	5.66	4.58	4.27	3.52	2.01[b]	
$[Fe(PBT)_2]_2O$	solid, 300	complex spectrum						
	solid, 77	complex spectrum			4.10		1.95[b]	
$[Fe(3\text{-}MePBT)_2]_2O$	solid, 300				4.18		2.07[b]	
	solid, 77		4.66		4.16		1.97[b]	
$[Fe(5\text{-}MePBT)_2]_2O\cdot\frac{1}{2}DMF$	solid, 77		4.75		4.15	2.25[a]	1.97[b]	
$[Fe(3\text{-}MeOPBT)_2]_2O\cdot CH_3CN\cdot H_2O$	solid, 300	5.44					2.06	
	solid, 77	8.76			4.23	2.54[a]	1.99[b]	
$[Fe(5\text{-}MeOPBT)_2]_2O\cdot 2H_2O$	solid, 300				4.27		2.08[a]	
	solid, 77	7.6	4.88		4.26		1.98[b]	
	DMF solution, 77		4.92	4.39	4.25			
$[Fe(3,4\text{-}MeOPBT)_2]_2O$	solid, 300				4.40		2.03[b]	
	solid, 77				4.28		2.02[b]	
	DMF solution, 77	7.79	5.69		4.22		1.79[a]	
$[Fe(4\text{-}NMe_2PBT)_2]_2O\cdot\frac{1}{2}CH_3OH$	solid, 300	7.37			4.29		2.01[b]	
	solid, 77	8.06	5.22	4.26	2.99	2.35	1.96	1.62
$[Fe(PMeBI)_2]_2(OH)_2\cdot 1\frac{1}{2}H_2O$	solid, 300						2.02[a]	
	solid, 77						2.05[a]	

[a]Broad band. [b]Sharp band.

dimers [10, 30, 31]. Due to exchange parameters for the compounds that are greater than the ESR microwave energies used, the molecules effectively have dimer electronic ground and excited states with total spin $S = 0, 1, 2, 3, 4, 5$. All the states other than the singlet ground state give rise to EPR signals.

The rest of the compounds gave spectra of varying degrees of complexity (Table 2), but often more akin to that of the mononuclear $Fe(PBT)_2Cl$. The signal at $g = 4.3$ is characteristic of tetragonally or rhombically distorted *monomeric* Fe(III) [31, 32] and is observed in almost all of the compounds. Its position is essentially independent of ligand composition. This signal is associated with the perpendicular transition in the $M_S = \pm\frac{1}{2}$ Kramers doublet observed when the zero-field splitting is greater than the EPR microwave energy ($> \sim 0.3$ cm^{-1} for X-band) [33].

However, there are spectral characteristics in some of the compounds which are difficult to rationalize as being due to simple high-spin Fe(III) species. We were unable to access sufficiently low temperatures (0–8 K) to completely depopulate the dimer $S > 0$ states and observe the spectra solely due to monomeric iron(III).

Sharp, weak resonances near $g = 2.00$ due to ligand radicals are observed in most of the compounds at low temperatures. This may be due to oxidation of the phenolate portion of the ligand by iron(III) in solution. Xu and Jordan [34] have observed oxidation of 2,3-dihydroxybenzoic acid in acidic aqueous solution. In some cases these bands become broader at room temperature suggesting spin–spin relaxation.

Electronic Absorption Spectra

The solid-state diffuse reflectance spectra showed strong absorptions beginning at around 1000 nm with the exception of $[Fe(4\text{-}Me_2NPBT)_2]_2O$ wherein the onset is about 1500 nm. These absorbances contain the electronic transition bands which appear as shoulders at around 850 nm and 550 nm (Table 3). These bands can be assigned to spin-forbidden d–d transitions by analogy with assignments for other binuclear iron(III) compounds [35, 36]. The higher energy ligand field bands are obscured by the more intense charge-transfer absorptions. These assignments are comparable to those for mononuclear iron(III) since the spin–spin coupling in the dimers is small compared to the energy of the d–d transi-

TABLE 3. Diffuse reflectance spectra

Compound	λ (nm)		
$[Fe(PBT)_2]_2O$	800[a]	700sh	560sh
$[Fe(3\text{-}MePBT)_2]_2O$	860[a]		560sh
$[Fe(5\text{-}MePBT)_2]_2O\cdot\frac{1}{2}DMF$	850[a]		580sh
$[Fe(5\text{-}MeOPBT)_2]_2O\cdot\frac{1}{2}H_2O$			600sh
$[Fe(3,4\text{-}MeOPBT)_2]_2O$		750sh	500sh
$[Fe(4\text{-}NMe_2PBT)_2]_2O\cdot\frac{1}{2}CH_3OH$		700sh[b]	
$[Fe(PMeBI)_2]_2(OH)_2\cdot 1\frac{1}{2}H_2O$			480sh[a]

[a]Weak. [b]Very broad.

TABLE 4. *Electronic absorption spectra*[a]

Compound	Color	Solvent	λ (nm)						
$Fe(PBT)_2Cl$	brown	DMF	~900 (0.12)	770sh (0.13)	600sh (0.34)	430sh (2.6)	380sh (6.0)	330 (26)	300sh (21) 290 (22)
$[Fe(PBT)_2]_2O$	brown	DMF	~900 (0.04)	770sh (0.06)	510sh (1.3)	430sh (3.0)	380sh (7.2)	335 (22)	300 (17) 293sh (16)
$[Fe(3\text{-}MePBT)_2]_2O$	red–brown	DMF	~900 (0.15)	780sh (0.09)	525sh (3.2)	430sh (13)	350sh (44)	335 (47)	307sh (53) 293 (55)
$[Fe(5\text{-}MePBT)_2]_2O\cdot\frac{1}{2}DMF$	brown	DMF	~900 (0.15)	770sh (0.12)	500sh (4.0)	425sh (14)		337 (51)	310sh (50) 292 (53)
$[Fe(3\text{-}MeOPBT)_2]_2O\cdot 3H_2O$[b]	black	DMF	~900 (0.04)	780sh (0.07)	520sh (4.8)	425sh (10)	360sh (25)	335sh (34)	300 (54)
$[Fe(5\text{-}MeOPBT)_2]_2O\cdot\frac{1}{2}H_2O$	green–brown	DMF	~900 (0.07)	830sh (0.08)	530sh (3.7)	430sh (3.5)	350 (37)		310sh (43) 294 (44)
$[Fe(3,4\text{-}MeOPBT)_2]_2O$	yellow–brown	DMF	~900 (0.25)	780sh (0.03)	530sh (0.8)	425sh (4.5)	345sh (19)	330 (25)	307sh (17) 295sh (15)
$[Fe(4\text{-}NMe_2PBT)_2]_2O\cdot\frac{1}{2}CH_3OH$	green–brown	DMF	~900 (0.25)		530sh (3.1)		376 (104)		313sh (41) 267 (57)
$[Fe(PBI)_2]_2O$	red–brown	DMF	~900 (0.08)	775sh (0.03)	490sh (4.0)		340 (76)		295 (59)
$[Fe(PMeBI)_2]_2(OH)_2\cdot 1\frac{1}{2}H_2O$	pale brown	insoluble							

[a]Band positions in nm; molar absorptivity ($\times 10^{-3}$) in $dm^3\ mol^{-1}\ cm^{-1}$ is given in parentheses. [b]$[Fe(3\text{-}MeOPBT)_2]_2(OH)_2\cdot 2H_2O$.

tions for high-spin iron(III) in an octahedral field (11 000–25 000 cm^{-1}) [37].

The lowest states for a d^5 system in an octahedral field are $^6A_{1g}$, $^4T_{1g}$, and $^2T_{2g}$, but $^4T_{1g}$ cannot lie lowest in energy. However, in the compounds reported here the geometry is most likely square pyramidal about each iron and the $^4T_{1g}$ state is split into three orbital singlets $^4A_2 + {}^4B_1 + {}^4B_2$ under C_{2v} so the ground state will be a quartet [38]. The assignment of C_{2v} geometry assumes a *trans* arrangement of ligand donor atoms about the iron which seems the most likely arrangement to minimize steric interactions between the benzothiazole groups.

The solution spectra (Table 4) for the compounds are in general agreement with the solid-state spectra. All compounds show a weak band at around 900 nm ($\epsilon = 40$–250), followed by a strong absorption beginning at about 800 nm with shoulders at various wavelengths up to the peak maximum at about 300 nm. Figure 5 displays the visible region of some representative spectra. The ligand field bands in the visible region are more intense than would be expected for a mononuclear iron(III) compound [39]. The exceptional intensity of these bands has been attributed to relaxation of the parity and spin selection rules resulting from antiferromagnetic coupling of the oxo-bridged iron(III) dimers, [37, 40] but coupling between the LMCT and d–d transitions also appears possible.

The large value of molar extinction coefficient seen for the absorptions in the 550, 430 and 350 nm regions of the solution spectra indicate that these are probably due to ligand-to-iron(III) charge-transfer bands [16, 17, 41, 42]. The dependence of the position of these bands on the nature of the ligands has been suggested as a possible probe for the active

Fig. 5. Optical absorption spectra in the visible region for: —— $[Fe(PBT)_2]_2O$, – – – $[Fe(3\text{-}MePBT)_2]_2O$, ····· $[Fe(3\text{-}MeOPBT)_2]_2O\cdot 3H_2O$. $M^{-1} = dm^3\ mol^{-1}$.

sites of non-heme iron phenolate proteins [16, 41, 42]. Further, a correlation has been found between the position of these LMCT bands and $E_{1/2}$ for the iron(III)/(II) redox step of a series of Fe(salen)X compounds where X is a substituted phenolate and salen is an ethylenebis(salicylidiniminate) [16]. These findings show that the changes in energy of the dπ orbitals in the iron(III) complex are a major factor in determining the redox potential.

It can also be seen that the energy of the LMCT band for the monomeric $Fe(PBT)_2Cl$ is significantly lower than that for its dimeric counterpart. This can be rationalized if the chloride ion has greater electron-withdrawing capacity than the $OFeL_2$ unit.

In general, model studies have been done on compounds with a phenolate type ligand and a separate nitrogen and or oxygen donor ligand wherein electron releasing substituents on the phenolate ligand shift the charge transfer bands to lower energy. On the other hand for electron-releasing substituents on the non-phenolate ligand, the shift in band position is to higher energy.

In the compounds reported here, the phenolate donor and the other donor atom are incorporated into the same ligand; the electron-donating substituents on the phenolate tend to shift the absorption of the lower energy band (near 550 nm) to lower energies while the benzimidazole ligand causes a blue shift in the band relative to its benzothiazole analogue. The red shift in the PBT series follows the observations from other iron phenolate compounds; the electron-releasing substituents raise the energy of the ligand frontier orbitals and narrow the ligand-to-metal gap. The position of the band near 430 nm shows a curious absence of dependence on the type of ligand. The higher energy band (near 350) shows a general increase in energy as electron-releasing groups are added. This suggests this band is a benzothiazole-to-iron charge transfer transition since the trend in the [Fe(salen)catecholate]$^+$ complexes is for the salen-to-iron charge transfer band to blue shift with electron-donating groups added to the catecholate [42]. Further, this band is known to be in the near UV region since Raman excitation of the salen vibrations requires the lowest wavelength available [42]. The higher energy bands around 335, 300, 290, 280, 255 and 220 nm are assigned as ligand $\pi \rightarrow \pi^*$ transitions. These assignments correlate well with band positions observed for the free ligands.

The lowest energy band of the free ligands appears to be somewhat sensitive to electron donating substituents with a shift to lower energy as methyl and methoxy groups are added. This is particularly noticeable in the case of the dimethylamino-substituted PBT. One can also observe a three- to four-fold increase in band intensity of the complexed ligand compared to free ligand for most of the compounds.

Redox Chemistry

The electrochemical results are summarized in Table 5 which contains data obtained from rotating electrode polarograms. This process is assigned as the $Fe^{III}{}_2 \rightarrow Fe^{III}Fe^{II}$ step. The values of $D\eta$ are consistent with this being a one electron process [43], so that both irons are not simultaneously reduced at the same potential. In cyclic voltammetry, the reductions are all irreversible, as indicated by the virtual absence of an anodic peak. Electrochemistry could not be performed on $[Fe(PBT)_2]_2O$ due to its limited solubility so we have no direct comparison. The reduction potentials of the methyl- and methoxy-substituted complexes have about the same value to within 70 mV. However $[Fe(4\text{-}Me_2NPBT)_2]_2O$ has a value of $E_{1/2}$ which is about 100 mV lower than the average value of the other reduction potentials, consistent with the expected effect of electron-releasing ligand substituents on the iron(III) reduction potential.

TABLE 5. Electrochemistry in DMF/$(NEt_4)(ClO_4)$

Electroactive species	$E_{1/2}$ (mV)[a]	$10^{13} \times D\eta$ (kg m s^{-2})[b]
$[Fe(3\text{-}MePBT)_2]_2O$	−1220	1.45
$[Fe(5\text{-}MePBT)_2]_2O$	−1220	1.54
$[Fe(3\text{-}MeOPBT)_2]_2O$	−1200	2.30
$[Fe(5\text{-}MeOPBT)_2]_2O$	−1260	1.46
$[Fe(3,4\text{-}MeOPBT)_2]_2O$	−1190	1.82
$[Fe(4\text{-}NMe_2PBT)_2]_2O$	−1330	2.61

[a]Values from rotating electrode polarography, uncorrected for iR drop. [b]Values from rotating electrode polarography, D = diffusion coefficient, η = absolute viscosity [44].

Conclusions

Three LMCT bands are observed for all the compounds studied. The lowest energy band is assigned as phenolate-to-iron charge transfer and the highest energy band as benzothiazole-to-iron charge transfer. The dependence of phenolate-to-iron CT band position on the nature of the phenolate donor ligand follows the trend observed previously, with electron-donating groups on the ligand shifting the band to lower energies. The shift of band position to higher energy with benzimidazole donor ligands compared to benzothiazole donors is possibly due to the stronger basicity of the benzimidazole ligand. The increased electron density contributed by the ligand would be expected to raise the energy of the metal electron molecular orbitals through an inductive effect. The benzothiazole-to-iron CT band is shifted to higher energy in the same series.

The correlation between the peak position of the phenolate **LMCT** band and the reduction potential for the six compounds analyzed is only weak.

The stable form of these compounds is the oxo-bridged dimer. Several attempts were made to synthesize the mononuclear bis- or tris-complexes with and without added base and with the use of dehydrating agents. We were successful in isolating a stable mononuclear product in the case of the **PBT** complex but only with the use of an auxiliary ligand.

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