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Article

A Phenolate-Induced Trans Influence: Crystallographic Evidence for Unusual Asymmetric Coordination of an α-Diimine in Ternary Complexes of Iron(III) Possessing Biologically Relevant Hetero-Donor N-Centered Tripodal Ligands

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Three mononuclear ternary complexes of iron(III) with an α-diimine (bipy or phen) and a derivative of *N*,*N*-bis(2-hydroxybenzyl)glycinate (L^{3-}) have been synthesized and characterized by magnetic susceptibility measurements, electron paramagnetic resonance (EPR) spectroscopy, vibrational spectroscopy, and electronic absorption spectroscopy. Single-crystal X-ray structure determinations of the pseudo-octahedral complexes [Fe(bipy)L]·MeCN [L = $(3,5\text{-}Br_2)\text{-}L^{3-}$ or $(5,3\text{-}Cl,Me)\text{-}L^{3-}$] revealed a considerable and consistent distortion in the coordination of bipy to iron(III) attributable largely to electronic effects. In both crystal structures, the $Fe–N_{pyridyl}$ bond trans to the phenolate oxygen is 0.133 Å longer than the other one positioned trans to the tertiary amine nitrogen, a relatively weaker donor. This coordination behavior of bipy is of structural interest and has not been observed previously for iron(III). The electronic and EPR spectra of the compounds [Fe(L′–L′)L]·MeCN (L′–L′ = bipy or phen) are consistent with the spin state of the central metal atom ($S = {}^5/_2$). The charge-transfer transitions arising from the strong interactions of the phenolate moieties with the ferric ion have been identified as phenolate (p_π) → iron(III) (d_{π^*}) ($\lambda_{max} \approx$ 500 nm, $\epsilon \approx$ 3000 M^{-1} cm^{-1}) and phenolate (p_π) → iron(III) (d_{σ^*}) ($\lambda_{max} \approx$ 320 nm, $\epsilon \approx$ 5200 M^{-1} cm^{-1}). The presence of the phenolate moieties in the quadridentate hetero-donor tripodal ligands, H_3L, lends these iron(III) ternary complexes the potential to model the specific metal-coordination, metal–substrate interactions, and physicochemical behaviors of several iron-tyrosinate proteins.

Introduction

In recent times, iron(III) complexes with N-centered quadridentate tripodal ligands comprising pyridyl,[1] phenolic,[2] carboxylic,[3] imidazole,[4] or benzimidazole[1d,5] "pendants" or combinations of these[1d,6] have attracted much attention due in part to their propensity to model the structural, physicochemical, and functional behaviors of a diverse range of metalloenzymes including the catechol dioxygenases,[7] purple acid phosphatases,[8] soybean lipoxygenases,[9] bacterial superoxide dismutases,[10] galactose oxidase,[11] and α-keto acid-dependent enzymes,[7a] and metalloproteins such as the transferrins.[12] Of particular relevance to the work presented herein are the catechol dioxygenases[7] and the transferrins,[12] the nonhaem iron-tyrosinate proteins possessing mononuclear bioactive centers (Figure 1[7c,12a,13,14]).

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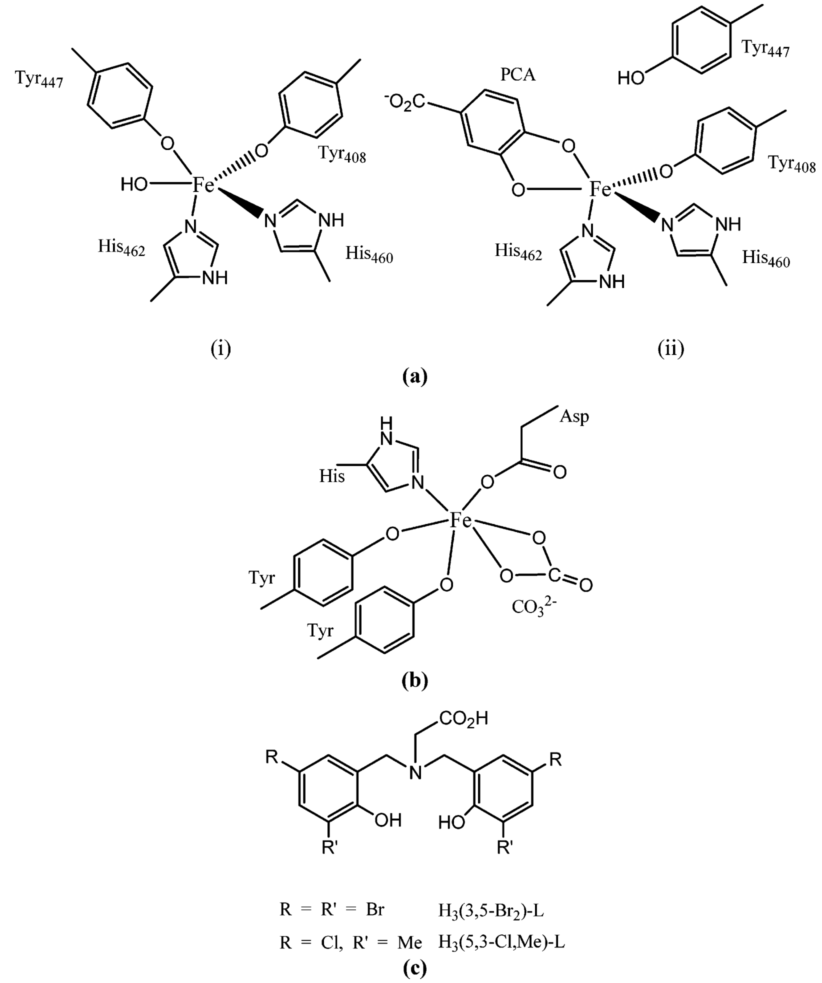
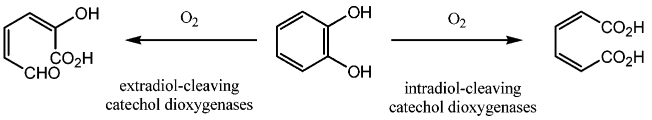


R = R' = Br H$_3$(3,5-Br$_2$)-L
R = Cl, R' = Me H$_3$(5,3-Cl,Me)-L

Figure 1. Schematic representations of (a) the active sites of (i) 3,4-PCD[7] and (ii) the 3,4-PCD-PCA intermediate,[13] and (b) one of the two specific metal-binding sites of human lactoferrin;[12a] (c) the structures and designations of the quadridentate tripodal ligands.[14]

Scheme 1. Modes of Oxidative Cleavage of Catechol



The catechol dioxygenases catalyze the biodegradation of catechols to aliphatic acids by oxidative cleavage of the aromatic rings of the former.[7,15] These bacterial enzymes are categorized either as intradiol-cleaving or as extradiol-cleaving catechol dioxygenases in accordance with the mode of cleavage (Scheme 1).[7,15] The intradiol-cleaving enzymes possess high-spin iron(III) in a distorted trigonal bipyramidal coordination environment at the catalytic sites and are exemplified by catechol 1,2-dioxygenase[16] and protocatechuate 3,4-dioxygenase (3,4-PCD).[7b,c] In contrast, the extradiol-cleaving enzymes contain iron(II) and are represented by catechol 2,3-dioxygenase,[17] 2,3-dihydroxybiphenyl dioxygenase (BphC),[7d,e] and protocatechuate 4,5-dioxygenase.[18]

Considering the mixed-atom-donor coordination environment of the active site of 3,4-PCD (four endogenous protein ligands: Tyr408, Tyr447, His460, and His462)[7c,13,19,20] [Figure 1a], it is surprising that the all-N-donor tripodal ligand tris-(2-pyridylmethyl)amine (TPA)[1] has been utilized extensively and successfully to model the physico-

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chemical and functional behaviors of the catechol dioxygenases. A structural feature of particular interest at the active site of 3,4-PCD is the asymmetric coordination of the anionic substrate 3,4-dihydroxybenzoate (commonly known as protocatechuate and denoted as PCA) to the metal center.[13] This asymmetric chelation of PCA causes dissociation of the endogenous axial Tyr447$-$Fe^{III} bond and allows ketonization of the substrate 3-position followed by electrophilic attack by O_2 at the substrate 4-position. In the PCA-bound 3,4-PCD intermediate (anaerobic 3,4-PCD-PCA complex), the average Fe$-$O$_{substrate}$ bond distances Fe$-$PCA^{O3} and Fe$-$PCA^{O4} are approximately 2.41 and 2.16 Å, respectively, clearly showing asymmetric coordination of the substrate.[13] The longer distance from the metal center is the one to the catecholate oxygen positioned very nearly trans to the strongly basic oxygen of Tyr408 (Tyr408$^{O\eta}$$-Fe-$PCA^{O3} $\approx$ 171°). In this crystallographic study, the asymmetry of the chelation of PCA was thought to arise from ligand constraints, hydrogen bonding between Arg457$^{N\eta1}$ and PCA^{O3}, and trans ligand influences.[13] However, the trans influences of the endogenous protein ligands were postulated to be the primary cause of this distortion.[21] The trans influence shortened the Fe$-$PCA^{O4} bond distance as His462$^{N\epsilon2}$ (opposite PCA^{O4}) accepted electron density and elongated the Fe$-$PCA^{O3} as Tyr408 donated electron density to the metal center.[13]

Highly reactive functional models for catechol 1,2-dioxygenases have been produced by several research groups, and these compounds include [Fe^{III}(NTA)DBC]$^{2-}$ (NTA = nitrilotriacetate; DBC = 3,5-di-*tert*-butylcatecholate),[3] [Fe^{III}(BPG)DBC] [BPG = *N*,*N*-bis(2-pyridylmethyl)glycine],[6b] [Fe^{III}(TPA)DBC]$^{+}$ [TPA = tris(2-pyridylmethyl)amine],[1a] [Fe^{III}(BPIA)TCC]$^{+}$ (BPIA = bis[(2-pyridyl)-methyl] [1-methylimidazol-2-yl)methyl]amine; TCC = tetrachlorocatecholate),[6g,k] and [Fe^{III}(L)TBC]$^{-}$ (L = variously substituted dinegative bis-phenolate tripodal ligands; TBC = tetrabromocatecholate).[6l] In [Fe^{III}(NTA)DBC]$^{2-}$, [Fe^{III}(BPG)DBC], [Fe^{III}(TPA)DBC]$^{+}$, and [Fe^{III}(BPIA)TCC]$^{+}$, the DBC and TCC ligands coordinate asymmetrically with the shorter Fe$-$O$_{catecholate}$ bond consistently being the one trans to the Fe$-$N$_{amine}$ bond. Que et al.[1a,3,6b] and Krebs et al.[6g,k,l] rationalized this mode of coordination of DBC and TCC by invoking the "trans effect", and, in the case of [Fe^{III}(NTA)DBC]$^{2-}$, steric constraints were ruled out as a contributing factor. Likewise, in the series of [Fe^{III}(L)TBC]$^{-}$ complexes, the TBC ligand coordinates in an asymmetric fashion. The Fe$-$O$_{catecholate}$ bond trans to the phenolate oxygen of the tripodal ligand is consistently longer than the other. Krebs et al.[6l] attributed this coordination behavior of TBC to the trans influences of the phenolate oxygens of the tripodal ligand. The trans influence of phenolate has also been demonstrated by the work of Yamahara et al.[6i] using the model complexes [Fe(L$_{H,H}$)DBC], [Fe(L$_{H,H}$)acac]$^{+}$ and [Fe(L$_{H,H}$)Cl$_2$] [HL$_{H,H}$ = 2-hydroxyphenyl-bis(2-pyridylmethyl)amine; acac = acetylacetonate].

This work investigates the reactivity of the *N*,*N*-bis(2-hydroxybenzyl)glycinate (L^{3-}) tripodal ligands[14] with the ferric ion and the subsequent chelation of the bipy or phen α-diimine. Each of the potentially quadridentate tripodal ligands *N*,*N*-bis(3,5-dibromo-2-hydroxybenzyl)glycine [H$_3$(3,5-Br$_2$)-L] and *N*,*N*-bis(5-chloro-2-hydroxy-3-methylbenzyl)glycine [H$_3$(5,3-Cl,Me)-L] [Figure 1c][14] possesses two phenolic oxygen atoms, one carboxyl oxygen atom, and one tertiary amine nitrogen atom for coordination. These polydentate ligands provide a hetero-donor-atom environment relevant to iron(III)$-$tyrosinate proteins, especially the catechol 1,2-dioxygenases[7] and the transferrins[12] (viz., lactoferrin,[12a,b] serum transferrin,[12c] and ovotransferrin[12d,e]) [Figure 1b]. However, in this preliminary study, we explore the ability of these tripodal ligands to form ternary complexes of iron(III) and their capacity to produce asymmetry in the coordination of the α-diimines of interest [2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen)]. The choice of bipy and phen in this study is two-pronged: first, the coordination of either of these bidentate ligands would lead to readily isolable electrically neutral complexes of iron(III), and, second, the equivalence of the pyridyl N donor atoms of these α-diimines would allow convenient manifestation of trans influences of the tripodal ligands on coordination to the ferric iron.

Mononuclear compounds of the divalent ions of ruthenium[22a,b] and platinum[22c] with α-diimines and/or their derivatives have drawn much attention recently as potential chromophoric constituents of photochemical molecular de-

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vices due in part to their favorable photophysical and redox properties. Ruthenium(II) polypyridyl complexes have been demonstrated to photoreact with DNA[23a] and to inhibit in vitro gene transcription.[23b] Our current interest in the bidentate α-diimines lies in the structural, magnetic, and spectroscopic features of their transition metal compounds possessing polydentate ligands. Crystallographically characterized iron(III) complexes of this kind are rare. In the vast majority of transition metal (M) compounds in which the two N donor atoms of the α-diimines (bipy and phen) occur in chemically equivalent environments or are both coordinated directly opposite to other donor atoms with no appreciable trans influence, the two M−N bonds tend to be equidistant or very nearly so; examples include $[Fe(bipy)_3]^{3+}$,[24a] $[Fe(phen)_3]^{3+}$,[24b] $[Co(phen)_3]^{3+}$,[24c] $[Ru(bipy)_2(Me\text{-}phen)]^{2+}$,[24d] $[Fe(phen)Cl_4]^-$,[24e] and $[Pt(bipy)(en)]^{2+}$.[22b] In contrast, the few known structurally elucidated oxovanadium(IV) complexes with one of the donor atoms of bipy or phen coordinated trans to the oxo group invariably show a large distortion of the α-diimine (typically, the two V−N bond distances are 2.10−2.17 and 2.30−2.35 Å).[25a−d] A modest trans influence of the bridging oxo group in oxo-bridged dinuclear vanadium(III) complexes such as $[V_2(\mu\text{-}O)(phen)_4Cl_2]^{2+}$ (V−N: 2.103 and 2.183 Å)[25e] has been reported.

In this paper, we report on, among other physical properties, the crystal structure determinations of the compounds of the type [Fe(bipy)L]·MeCN, which have revealed a distortion in the coordination of the bidentate bipy ligand to iron(III), the magnitude of which is comparable to that observed in α-diimine-containing oxovanadium(IV) complexes.[25a−d] A comprehensive crystallographic search for ternary complexes of iron(II/III) with bipy together with any polydentate ligand yielded no results, and thus the asymmetric coordination of bipy reported herein is considered to be observed for the first time for iron(III). The only other compound of iron(III) that showed a large distortion of an iron-bonded bidentate α-diimine is $[Fe\{N(CH_2\text{-}o\text{-}C_6H_4O)_3\}(phen)]$,[2] but the asymmetric coordination of phen in this compound was explained in terms of a short contact between a benzyl proton and the hydrogen atom ortho to the phen N atom affected.

Scheme 2. Synthetic Route to the Complexes [Fe(L′-L′)L]·MeCN, **1**−**3**[a]

$$H_3L \xrightarrow[\text{MeCN/MeOH/EtOH}]{3Et_3N} L^{3-} \xrightarrow{Fe^{3+}} \text{"}[Fe(solv)_nL]\text{"} \xrightarrow{L'\text{-}L'} [Fe(L'\text{-}L')L].MeCN$$

[a] H_3L = quadridentate tripodal ligand; L′−L′ = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen); solv = solvent molecule; *n* = 1 or 2.

Results and Discussion

Synthetic Route to Complexes. Typically, iron(III) binds to a quadridentate tripodal ligand and an additional monodentate ligand to give a distorted trigonal bipyramidal geometry,[2,7,13] or to a quadridentate tripodal ligand along with two monodentate ligands or one bidentate ligand to give a pseudo-octahedral geometry.[1−6] So far, we have focused our research on electrically neutral complexes of iron(III) with the quadridentate ligands $(3,5\text{-}Br_2)\text{-}L^{3-}$ or $(5,3\text{-}Cl,Me)\text{-}L^{3-}$ using the α-diimines bipy or phen to produce six-coordinate species. The compounds $[Fe(bipy)(3,5\text{-}Br_2)\text{-}L]\cdot MeCN$ (**1**·MeCN), $[Fe(phen)(3,5\text{-}Br_2)\text{-}L]\cdot MeCN$ (**2**·MeCN), and [Fe(bipy)(5,3-Cl,Me)-L]·MeCN (**3**·MeCN) were synthesized in a solvent mixture of MeOH/EtOH/MeCN according to Scheme 2.

The complexes "$[Fe(solv)_nL]$" were not isolated, but their formation was indicated by the intense colors developed on reaction of the metal ion with the trinegative ligand anions. These complexes can be five-coordinate as in the crystallographically characterized complex $[Fe\{N(CH_2\text{-}o\text{-}C_6H_4O)_3\}(DMF)]$[2] or six-coordinate as exemplified structurally by the iron(II) complexes $[Fe(TPA)(MeCN)_2]^{2+}$ and $[Fe(TPA)(MeOH)_2]^{2+}$.[26] Although iron(III) complexes with quadridentate tripodal ligands have a tendency to form trigonal bipyramidal geometries in the presence of monodentate ligands, octahedral complexes of iron(III) containing such tripodal ligands and two monodentate ligands are known.[1b,d,4,6d,e,h,i,k]

The isolation of ternary complexes containing bipy or phen ligands is unusual due to the driving force for forming the $[M(bipy)_3]^{n+}$ or $[M(phen)_3]^{n+}$ complexes.[27] Examples of mixed-ligand complexes with bipy or phen include $[Fe(bipy)(Cl_4Cat)_2]^-$ (Cl_4Cat^{2-} = TCC = tetrachlorocatecholate),[27] $[Fe(bipy)_2(C_2O_4)]$,[28] $[Cu(bipy)(C_2O_4)]$,[29] [Cu(sgly)phen] [sgly = *N*-(2-hydroxybenzyl)glycinate],[30] $[Co(DPG)phen]^{2+}$ [NB: DPG = BPG = *N*,*N*-bis(2-pyridylmethyl)glycinate],[31] [VO(sala)bipy] (sala = *N*-salicylidene-L-alaninate),[25b] and [VO(L)bipy] [L = *S*-methyl-3-(2-hydroxy-5-nitrophenyl)-methylenedithiocarbazate].[25d] In this study, the isolation of

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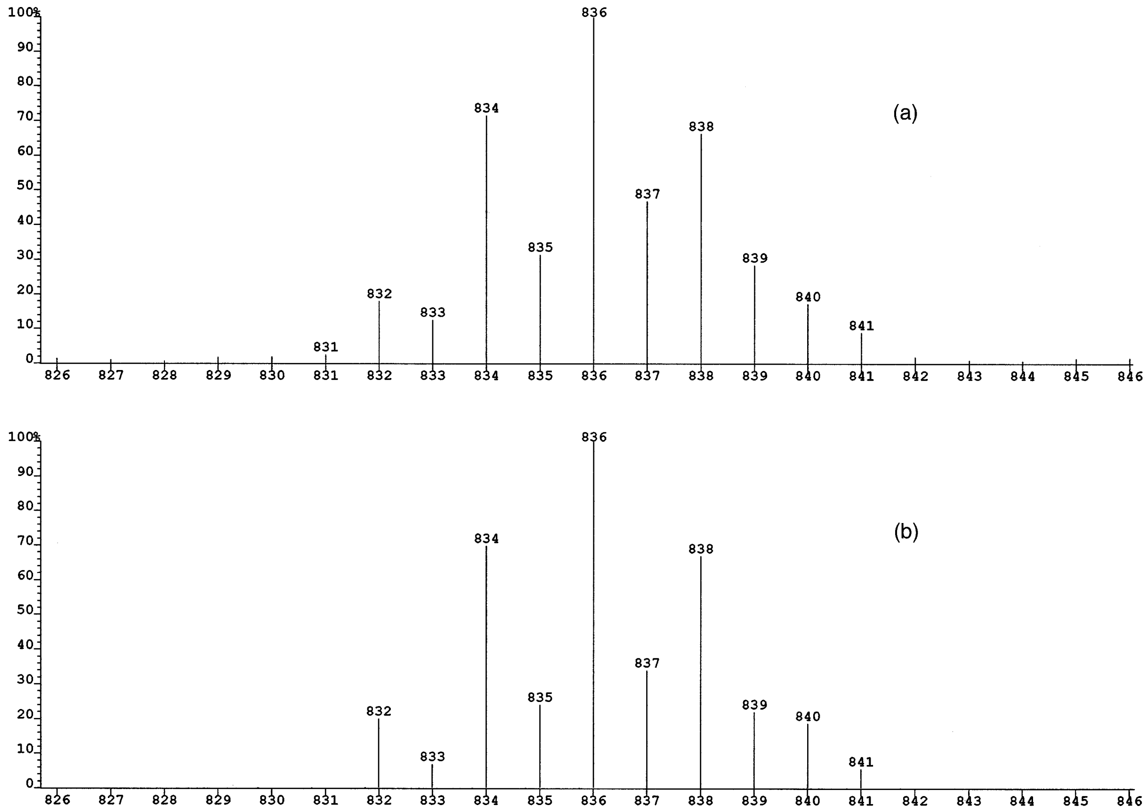

Figure 2. (a) Observed and (b) simulated isotopic distribution patterns of [Fe(phen)(3,5-Br_2)-L] **2** in the molecular envelope.

the complexes [Fe(L′−L′)L]·MeCN (L′−L′ = bipy or phen) can be rationalized by the strong binding of the quadridentate trianionic ligands to the iron(III); thus, the incoming bipy or phen ligand does not displace L^{3-}, but rather binds to the remaining sites, and the neutral complexes are favorably precipitated from solution. Other crucial factors include the stoichiometry of the reactants and the synthetic route.

Upon controlled evaporation of the solvent mixture, compounds **1**·MeCN and **2**·MeCN crystallized as reddish-purple rectangular blocks, whereas **3**·MeCN was isolated as black-purple bocks. Conductivity measurements in MeOH verified that these compounds are nonelectrolytes and that they remain intact in solution. The chemical compositions were established by microanalyses (C, H, and N) and FAB mass spectrometry. The molecular ions $[Fe(L'-L')L]^+$ were identified by their peaks at *m*/*z* 812, 836, and 593 for **1**·MeCN, **2**·MeCN, and **3**·MeCN, respectively. Furthermore, prominent peaks in the FAB mass spectra revealed the fragmentation pattern that began with the loss of the carboxylate group, followed by loss of one of the substituted phenolic rings, then the amine-phenolic unit, and finally the α-diimine ligand. The simulated isotopic distribution pattern for the molecular envelope of peaks matched closely the observed one. (A portion of the mass spectrum of **1**·MeCN is given in Figure 2 to illustrate this point.)

Magnetic Properties. The magnetic susceptibilities of **1**·MeCN, **2**·MeCN, and **3**·MeCN were recorded over the temperature range 5−300 K. The magnetic behavior of **1**·MeCN, displayed in Figure 3 (χ_M^{-1} vs T), shows normal paramagnetism and is in conformity with the Curie−Weiss law [$\chi_M = C/(T-\theta)$]; it is also representative of the magnetic properties of the other two compounds in this system. The Weiss constants of these three compounds are virtually identical ($\theta \approx 0.8$ K for **1**·MeCN, ~1.0 K for **2**·MeCN, and ~0.9 K for **3**·MeCN) and indicate that in each compound the iron(III) centers are by and large magnetically independent of one another. The room-temperature effective magnetic moments [$\mu_{eff} = (8\chi_M T)^{1/2}$] of the compounds **1**·MeCN, **2**·MeCN, and **3**·MeCN are 5.91, 5.88, and 5.90 μ_B, respectively, consistent with a high-spin d^5 configuration ($S = {}^5/_2$) for the iron(III) atom [spin-only paramagnetism: $\mu_{eff} = \{4S(S+1)\}^{1/2}$].[32] Indeed, mononuclear octahedral complexes of iron(III) with donor-atom sets comprising a combination of oxygen and nitrogen atoms tend to be spin-free at room temperature.

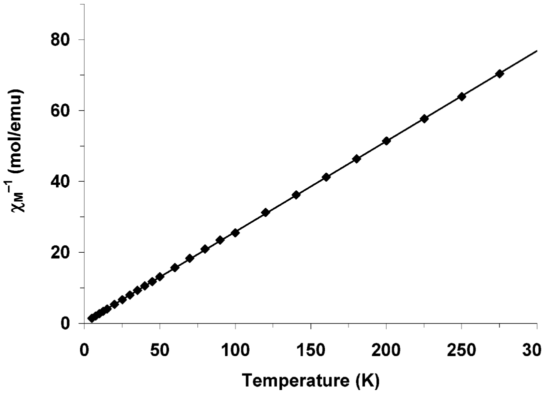

Figure 3. The variation of χ_M^{-1} for [Fe(bipy)(3,5-Br_2)-L]·MeCN as a function of temperature.

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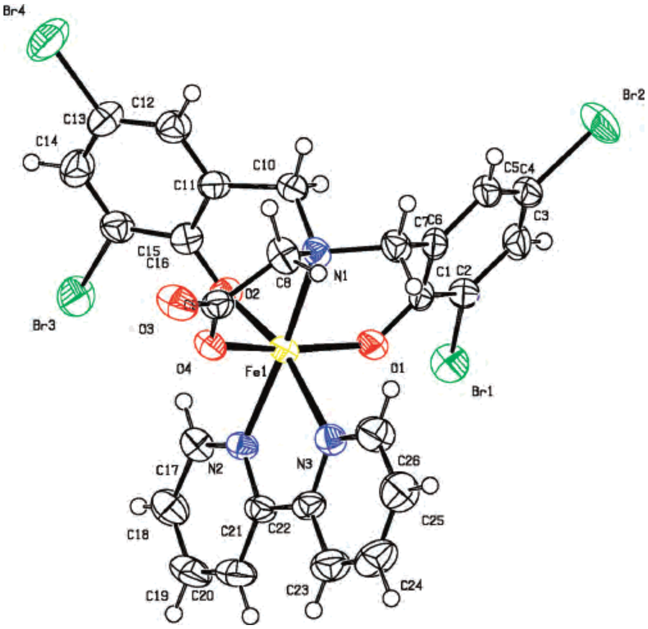

Figure 4. X-ray crystal structure of [Fe(bipy)(3,5-Br_2)-L]·MeCN (**1**·MeCN).

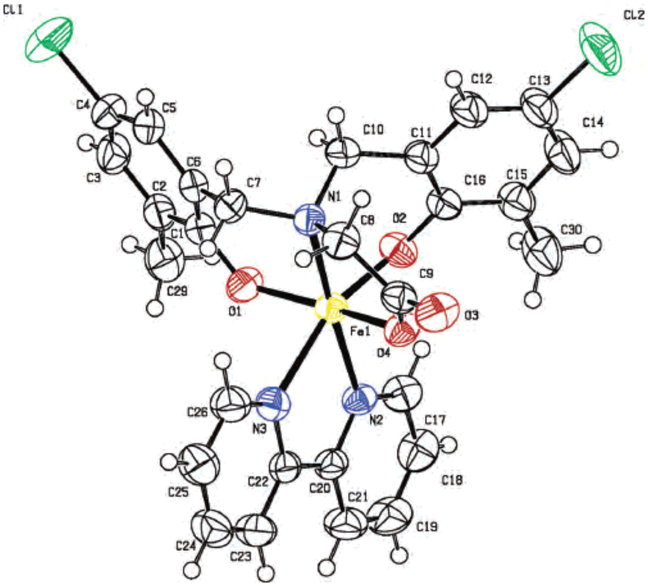

Figure 5. X-ray crystal structure of [Fe(bipy)(5,3-Cl,Me)-L]·MeCN (**3**·MeCN).

Table 1. Selected Bond Distances (Å) and Angles (deg) for [Fe(bipy)(3,5-Br_2)-L]·MeCN and [Fe(bipy)(5,3-Cl,Me)-L]·MeCN

[Fe(bipy)(3,5-Br_2)-L]·MeCN		[Fe(bipy)(5,3-Cl,Me)-L]·MeCN	
Fe1−O1	1.887(3)	Fe1−O1	1.887(2)
Fe1−O2	1.934(4)	Fe1−O2	1.915(2)
Fe1−O4	2.001(3)	Fe1−O4	1.997(2)
Fe1−N1	2.222(4)	Fe1−N1	2.217(2)
Fe1−N2	2.132(4)	Fe1−N2	2.152(2)
Fe1−N3	2.265(5)	Fe1−N3	2.285(3)
C27−C28	1.431(14)	C27−C28	1.432(7)
C27−N4	1.106(12)	C27−N4	1.116(6)
O1−Fe1−O4	161.74(15)	O1−Fe1−O4	161.14(10)
O2−Fe1−N3	163.96(15)	O2−Fe1−N3	162.50(9)
N1−Fe1−N2	171.65(15)	N1−Fe1−N2	173.22(9)
O1−Fe1−O2	99.57(16)	O1−Fe1−O2	101.30(10)
O2−Fe1−O4	92.12(16)	O2−Fe1−O4	92.74(9)
O1−Fe1−N2	100.19(15)	O1−Fe1−N2	97.64(9)
O2−Fe1−N2	90.84(16)	O2−Fe1−N2	90.53(9)
O4−Fe1−N2	93.56(14)	O4−Fe1−N2	94.73(9)
O1−Fe1−N1	87.56(15)	O1−Fe1−N1	88.38(9)
O2−Fe1−N1	90.95(15)	O2−Fe1−N1	91.36(9)
O4−Fe1−N1	78.22(14)	O4−Fe1−N1	78.68(8)
O1−Fe1−N3	87.81(16)	O1−Fe1−N3	87.50(10)
O4−Fe1−N3	84.55(16)	O4−Fe1−N3	82.50(9)
N2−Fe1−N3	73.77(16)	N2−Fe1−N3	73.20(10)
N1−Fe1−N3	103.65(16)	N1−Fe1−N3	104.09(9)
C28−C27−N4	179.1(15)	C28−C27−N4	178.7(7)

X-ray Crystallography. Crystals of these compounds suitable for single-crystal X-ray crystallography were obtained from a solvent mixture of MeOH/EtOH/MeCN by ether diffusion at room temperature, and the crystallization seemed to be sensitive to the metal salt used (preferring NO_3^- over ClO_4^- or Cl^- as its Fe^{III} salt) and the synthetic route followed. The X-ray crystal structures of **1**·MeCN and **3**·MeCN were determined at room temperature and are depicted in Figures 4 and 5, respectively. Selected bond distances and angles are listed in Table 1. The structures of the two compounds are very similar; in each case, the deprotonated tripodal ligand, L^{3-}, is coordinated to the iron(III) center in a quadridentate manner via two phenolate oxygen atoms, one carboxyl oxygen atom and one tertiary amine nitrogen atom. The pseudo-octahedral geometry around the metal ion is completed by the bidentate bipy molecule, which coordinates in the equatorial plane. The deviation of the coordination sphere from O_h symmetry is evident in the bond angles that differ from 90° by 0.53−16.80° and from 180° by 6.78−18.86°. Likewise, the bond distances are all different, this being a consequence of the inherent coordination requirements of each donor atom and the stereochemical constraints imposed by the polydentate ligand. Although not shown in Figures 4 and 5, in close proximity to each complex, [Fe(bipy)L], there exists an acetonitrile solvent molecule.

The bond distances Fe1−O1 [1.887(3) Å] and Fe1−O2 [1.934(4) Å] for **1**·MeCN and Fe1−O1 [1.887(2) Å] and Fe1−O2 [1.915(2) Å] for **3**·MeCN are normal for interactions between a high-spin iron(III) center and phenolate oxygen donor atoms in a six-coordinate environment. Typically, high-spin iron(III)−$O_{phenolate}$ distances range from 1.88 to 1.93 Å.[33] Likewise, the bond distances Fe1−$N1_{amine}$ [2.222(4) Å for **1**·MeCN and 2.217(2) Å for **3**·MeCN] and Fe−$O4_{carboxyl}$ [2.001(3) Å for **1**·MeCN and 1.997(2) Å for **3**·MeCN)] are comparable to those observed in related tripodal ligands (Fe−N_{amine} ≈ 2.16−2.38 Å[1−6] and Fe−$O_{carboxyl}$ ≈ 1.95−2.09 Å[6b,e,34]). Although chemically equivalent in the uncoordinated ligand, the pyridyl nitrogen atoms of bipy in **1**·MeCN coordinate to the iron(III) atom asymmetrically with one normal Fe−$N_{pyridyl}$ bond distance [Fe1−N2 2.132(4) Å][24e,35] and the other significantly longer [Fe1−N3 2.265(5) Å].[2] The same structural behavior was observed in **3**·MeCN [Fe1−N2 2.152(2) Å vs Fe1−N3

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2.285(3) Å]. Interestingly, the differences in the Fe$-$N$_{\text{pyridyl}}$ distances of the bipy ligands in the two compounds are identical (0.133 Å) and compare favorably with those observed in oxovanadium(IV) complexes.[25a−d] This lengthening can be ascribed primarily to the trans influence of the strongly basic phenolate oxygen atom whose strong π- and pseudo-σ-bonding to the metal center considerably weakens the coordination of the pyridyl nitrogen directly opposite it. This strong phenolate$-$iron(III) interaction is borne out by the charge-transfer absorptions of these compounds. The trans influence of a phenolate moiety, leading to asymmetry of the coordination of a bidentate ligand, has been demonstrated by the intermediate enzyme complex 3,4-PCD-PCA[13] and a few synthetic model systems[6i,l] for the catechol 1,2-dioxygenases. For example, in the model complexes of Yamahara et al.,[6i] [Fe(L$_{\text{H,H}}$)(DBC)] and [Fe(L$_{\text{H,H}}$)(acac)]$^+$ [HL$_{\text{H,H}}$ = 2-hydroxyphenyl-bis(2-pyridylmethyl)amine; acac = acetylacetonate], the oxygen atom (of each bidentate ligand) trans to the phenolate oxygen of the tripodal ligand was lengthened significantly [Fe$-$O$_{\text{DBC}}$, 1.961(3) Å vs 1.890(3) Å; Fe$-$O$_{\text{acac}}$, 2.018(4) Å vs 1.907(4) Å]. A similar observation was made by Krebs et al.[6l] for the complexes [FeL(TBC)]$^-$ (L^{2-} = a bis-phenolate tripodal ligand; TBC = tetrabromocatecholate). It is noteworthy that the trans influence of phenolate is not restricted to complexes of iron(III) with tripodal ligands; for example, in the distorted square pyramidal copper(II) complex [Cu(sgly)phen] [sgly = *N*-(2-hydroxybenzyl)glycinate],[30] the phen ligand is asymmetrically coordinated in the equatorial plane with Cu$-$N bond distances of 2.071(7) and 2.004(6) Å, the longer bond being trans to the phenolate oxygen.

On the other hand, the other Fe$-$N$_{\text{pyridyl}}$ bond (in **1**·MeCN and **3**·MeCN) opposite the tertiary amine nitrogen, a much weaker donor than the phenolate oxygen, is consistently shorter. Interestingly, this structural feature (weak Fe$-$N$_{\text{amine}}$ bonding) is the hallmark of iron(III) complexes with N-centered tripodal ligands. In the pseudo-octahedral complex of iron(III) with the potentially heptadentate N-centered tripodal Schiff-base ligand, tris-[*N*-(salicylidene)-2-aminoethyl)]amine,[36] the tertiary amine nitrogen is not even coordinated to the metal center.

A closer inspection of the crystal structures of [Fe(bipy)L]·MeCN (**1**·MeCN and **3**·MeCN) revealed the possibility of repulsive intramolecular H···H interactions in the vicinity of the coordination sphere somewhat affecting the Fe$-$N$_{\text{pyridyl}}$ bond distances. The interactions C26$-$H26···H7 (2.132 Å) in **1**·MeCN and C26$-$H26···H7 (2.170 Å) in **3**·MeCN show short contacts between the aforementioned hydrogen atoms that could lead to lengthening of the same Fe$-$N$_{\text{pyridyl}}$ bond of bipy affected by the trans influence of the phenolate oxygen. As indicated previously,[2] it has been shown that in the complex [Fe{N(CH$_2$-*o*-C$_6$H$_4$O)$_3$}(phen)], the phen ligand has a distinctly asymmetric coordination with Fe$-$N$_{\text{pyridyl}}$ bond lengths of 2.158(7) and 2.340(7) Å; however, Koch et al. attributed this distortion solely to a short contact between a benzyl proton of the tripodal ligand and the hydrogen atom adjacent to the phen N atom affected. In view of the well-documented prevalence of ligand trans influences in small-molecule coordination compounds[1−6,25,30,31] and naturally occurring systems,[7,13,19−21] the trans influence of phenolate may also be another factor contributing to the lengthening of one of the Fe$-$N$_{\text{phen}}$ bonds [2.340(7) Å] in [Fe{N(CH$_2$-*o*-C$_6$H$_4$O)$_3$}(phen)].[2]

Interestingly, there is evidence that an electronic effect is also observable in systems that do not contain phenolate ligands. For instance, in the complexes [Fe(TPA)Cl$_2$]$^+$,[1b] [Fe(BPIA)Cl$_2$]$^+$ (BPIA = bis[(2-pyridyl)methyl][(1-methylimidazol-2-yl)methyl]amine),[6h] and [Fe(BIPA)Cl$_2$]$^+$ (BIPA = bis[(1-methylimidazol-2-yl)methyl][(2-pyridyl)methyl]amine),[6h] the Fe$-$Cl bond trans to the tertiary amine nitrogen is shorter than the other bond opposite an aromatic nitrogen; in the complexes [Fe(NTA)(DBC)]$^{2-}$,[3] [Fe(BPG)(DBC)],[6b] and [Fe(TPA)(DBC)]$^+$,[1a] the shorter Fe$-$O$_{\text{DBC}}$ bond was postulated to result from the weak Fe$-$N$_{\text{amine}}$ interaction in the trans position. Congruent with [Fe(BPG)(DBC)],[6b] [Co(DPG)phen]$^{2+}$ [DPG = *N*,*N*-bis(2-pyridylmethyl)glycinate][31] shows a shorter Co$^{\text{III}}$$-N_{\text{phen}}$ bond [1.919(3) Å] opposite the tertiary amine nitrogen as compared to the other [2.010(3) Å] trans to the carboxylate oxygen. In the dinuclear tripodal complex [Fe$_2$O(NTB)Cl$_2$]$^{2+}$ (NTB = tris[(benzimidazol-2-yl)methyl]amine),[5b] the benzimidazole ligand bonded trans to the bridging oxo group has a longer Fe$-$N bond distance associated with the trans influence of the oxo group.

Whereas there is a growing number of ternary complexes of iron(III) containing different forms of tripodal ligands and variously substituted catecholate ligands,[1a,3,6b,g,i,k,15] the corresponding iron(III) compounds with an α-diimine instead of catecholate are few and far between. To our knowledge, this is the first observation of a phenolate-induced distortion of the coordination of bipy to iron(III). As expected, both Fe$-$N$_{\text{pyridyl}}$ distances are much longer than those observed for low-spin Fe(III) [e.g., ∼1.96(3) and ∼1.97(3) Å in [Fe(bipy)$_3$]$^{3+}$ [24a] and [Fe(phen)$_3$]$^{3+}$,[24b] respectively]. The bipy bite angles N2$-$Fe1$-$N3 73.77(16)° and 73.20(10)° in **1**·MeCN and **3**·MeCN, respectively, are comparable to those reported for α-diimines in high-spin iron(III) compounds,[2,24e,27,35,37] but, as expected, differ significantly from those encountered in the low-spin complex cations [Fe(bipy)$_3$]$^{3+}$ [24a] and [Fe(phen)$_3$]$^{3+}$ [24b] (N$-$Fe$-$N averages ∼82.3° and ∼83.0°, respectively). Whereas the cause of the observed asymmetric coordination of bipy in **1**·MeCN and **3**·MeCN would seem to be principally electronic in nature, it would appear that in the complex cations [(bipy)AuPPh$_3$]$^+$ [38a] [Au$-$N$_{\text{pyridyl}}$: 2.166(2) and 2.406(2) Å], [PtCl(PEt$_3$)$_2$(η^1-phen)]$^+$,[38b] and [Pd(η^1-phen)(phen)(CH$_2$NO$_2$)]$^+$,[38c] this behavior was imposed on the α-diimines as a means to meet the stereochemical demands of the central metal ion.

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Table 2. Selected IR Spectroscopic Data for the Complexes [Fe(L′−L′)L]·MeCN (**1**·MeCN, **2**·MeCN, and **3**·MeCN)

	complexes		
vibrations (cm^{-1})	**1**·MeCN	**2**·MeCN	**3**·MeCN
$\nu_{as}(CO_2^-)$	1653	1652	1654
$\nu_s(CO_2^-)$	1339	1339	1339
$\nu(C-O)_{phenolate}$	1245, 1269	1243, 1270	1249, 1295
$\nu(C-N)_{pyridyl}$	1599	1598	1597
$\nu(C-C)_{aromatic}$	1432−1576	1427−1578	1413−1575
$\nu(C-H)_{aliphatic}$	2850−2941	2851−2942	2848−2947
$\nu(C-H)_{aromatic}$	3061	3058	3053

Infrared Spectroscopy. Selected IR absorptions for **1**·MeCN, **2**·MeCN, and **3**·MeCN are summarized in Table 2. A structural feature of importance in these complexes is the coordination mode of the carboxylate groups of L^{3-} which was shown in the X-ray structures of **1**·MeCN and **3**·MeCN to be monodentate and has subsequently been corroborated by the solid-state IR spectroscopic data [$\nu_{as}(CO_2^-) - \nu_s(CO_2^-) = \Delta\nu(CO_2^-)$: 314 cm^{-1} for **1**·MeCN, and 313 cm^{-1} for **2**·MeCN, and 315 cm^{-1} for **3**·MeCN].[39] The stretching frequencies of the carboxylate groups and the C−O of the phenolate moieties (Table 2) closely match those reported by Wieghardt et al.[39b] for the related complex of iron(III) with 4-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1-acetate(2−).

EPR Spectroscopy. The $^6A_1$ electronic ground state for Fe(III) in **1**−**3** ascertained from the magnetic studies of these compounds was confirmed by EPR spectroscopy. The X-band EPR spectra were recorded in frozen DMSO solution at 100−103 K. The spectrum of **1**·MeCN exhibits an intense resonance at $g = 4.28$ and a weaker one at $g = 8.90$. Generally, the resonance at $g \approx 4.3$ is observed in rhombically distorted high-spin Fe(III) complexes and is predicted to occur as the ratio of the zero-field splitting parameters E/D approaches $^1/_3$, the rhombic limit.[40] The EPR spectra of **2**·MeCN ($g = 4.27$ and 8.90) and **3**·MeCN ($g = 4.29$ and 8.88) are hardly distinguishable from that of **1**·MeCN, implying that these complexes have similar coordination environments. Although the g values of the resonances of these compounds are very close to those observed for the transferrins, there is splitting in the $g = 4.3$ resonance for the metalloproteins.[41] That this resonance is sensitive to the nature of the donor environment for the iron(III) atom has been amply demonstrated by our previous work on bovine lactoferrin[42] and that of others on human serum transferrin.[41b] The coordination environment of **1**−**3** differs from that of the transferrins in having bipy or phen instead of a carbonate ion and a tertiary amine instead of an imidazole.[12]

Electronic Spectroscopy. The violet color of [Fe(bipy)-(3,5-Br$_2$)-L]·MeCN and [Fe(phen)(3,5-Br$_2$)-L]·MeCN and the purplish violet color of [Fe(bipy)(5,3-Cl,Me)-L]·MeCN in methanol were associated with the visible absorptions in the electronic spectra of these compounds. To make a complete and unambiguous assignment of the bands in both the UV and the visible regions of the spectra, the reactions were monitored by UV−visible spectroscopy, the result of which is exemplified by the synthesis of [Fe(bipy)(5,3-Cl,-Me)-L] in methanol. The ligand H$_3$(5,3-Cl,Me)-L was deprotonated with 3 molar equiv of Et$_3$N in methanol, and the electronic spectrum of the resultant ligand anion was recorded [Figure 6a]. An equivalent amount of Fe(NO$_3$)$_3$·9H$_2$O was then added to the colorless solution of the ligand anion, producing a purplish violet solution instantaneously. The product of this reaction was tentatively formulated as "[Fe(solv)$_n$(5,3-Cl,Me)-L]" for convenience (assuming that the two vacant sites at the metal center were occupied by solvent molecules, possibly one[2] or two[26] per complex molecule). The electronic spectrum of this complex was measured and compared to that of the uncoordinated ligand anion [Figure 6a]. Finally, on reaction of the bidentate ligand, bipy, with the complex "[Fe(solv)$_n$(5,3-Cl,Me)-L]", the color of the solution darkened somewhat, but remained essentially purplish violet. The electronic spectrum of the complex [Fe(bipy)(5,3-Cl,Me)-L] is given in Figure 6b.

The intense band at 288 nm ($\epsilon = 24\,900$ M^{-1} cm^{-1}) and the shoulder at 238 nm ($\epsilon = 26\,900$ M^{-1} cm^{-1}) in the UV region of the spectrum of "[Fe(solv)$_n$(5,3-Cl,Me)-L]" coincided with those in the spectrum of the uncoordinated ligand anion, suggesting that the corresponding electronic transitions are ligand-centered. The lower-energy intraligand electronic transition is commonly observed in phenolate-containing iron(III) complexes[19] and iron-tyrosinate proteins (e.g., the transferrins),[41] and its origin is thought to be $\pi \rightarrow \pi^*$ in nature.[39b,41,43] Between 315 and 750 nm, the UV−visible spectra of "[Fe(solv)$_n$(5,3-Cl,Me)-L]" and [Fe(bipy)(5,3-Cl,-Me)-L] are virtually identical; each exhibits a shoulder at 325 nm ($\epsilon = 5200$ M^{-1} cm^{-1}) and a band at 515 nm ($\epsilon = 3100$ M^{-1} cm^{-1}). Because these absorptions were absent from the spectrum of the ligand anion and occurred in the complexes regardless of the presence or absence of bipy or phen, and given the fact that ligand-field transitions in high-spin iron(III) octahedral complexes are spin-forbidden, the electronic transitions in question would, therefore, appear to arise from interaction of the phenolate oxygen with the iron(III) ion. The spectra of "[Fe(solv)$_n$(5,3-Cl,Me)-L]" and [Fe(bipy)(5,3-Cl,Me)-L] resemble that of [Fe(EDDHA)]$^-$ [EDDHA^{4-} = ethylenediamine di(*o*-hydroxyphenylacetate)][43a] except that the entire spectra of the former complexes are

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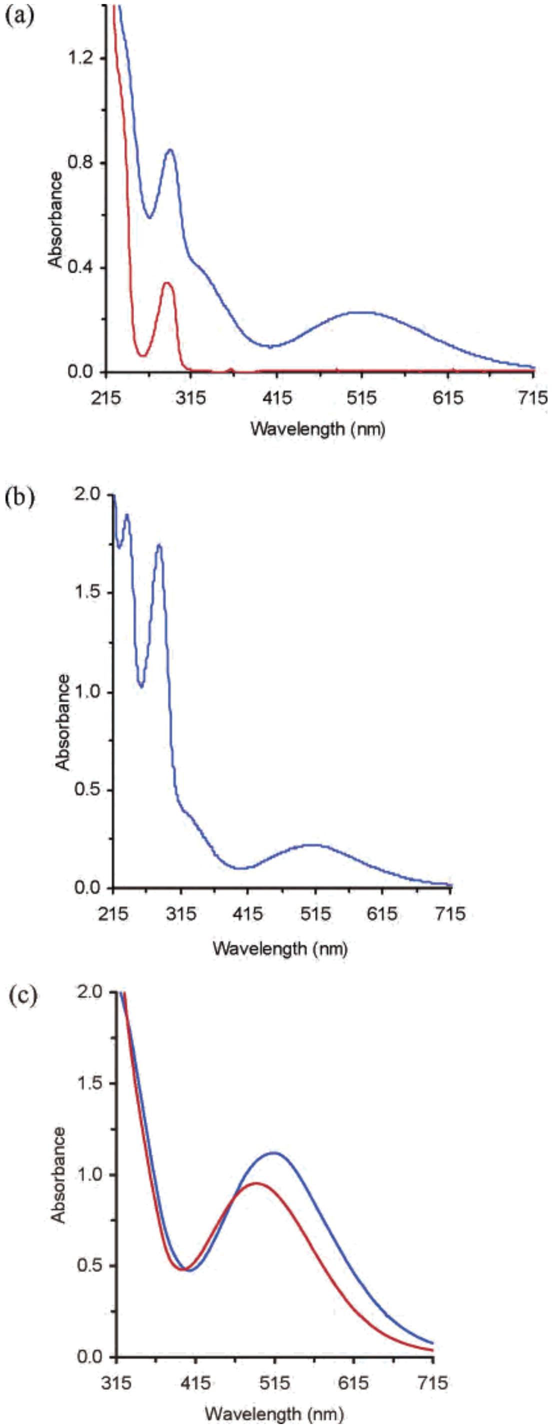

Figure 6. (a) Electronic spectra of [(5,3-Cl,Me)-L]$^{3-}$ (purple line) and "[Fe(solv)$_n$(5,3-Cl,Me)-L]" (blue line) in MeOH at a concentration of 0.070 mM; (b) electronic spectrum of [Fe(bipy)(5,3-Cl,Me)-L]·MeCN in MeOH at a concentration of 0.070 mM; (c) visible spectra of [Fe(bipy)-(3,5-Br$_2$)-L]·MeCN (purple line) and [Fe(bipy)(5,3-Cl,Me)-L]·MeCN (blue line) in MeOH at a concentration of 0.35 mM.

red-shifted. The visible absorption band is ascribed to a phenolate (p$_\pi$) → iron(III) (d$_{\pi*}$) charge-transfer transition, and its intensity (ϵ/phenolate = 1550 M^{-1} cm^{-1}) is consistent with this assignment.[43] The shoulder at 325 nm is attributed to a charge-transfer transition from the phenolate p$_\pi$ orbital to the d$_{\sigma*}$ orbital of Fe^{III}.[41b,43a,44] The difference in the energies of these LMCT bands (10 900 cm^{-1}) is an approximate measure of Δ_o for the complex [Fe(bipy)(5,3-Cl,Me)-L]. Examples of related complexes which show similar electronic features are [Fe(EDDHA)]$^-$ (LMCT bands: 315 and 475 nm, $\Delta_o \approx$ 10 700 cm^{-1})[43a] and [Fe(bbpen)]$^+$ [H$_2$bbpen = *N*,*N'*-bis(2-hydroxybenzyl)-*N*,*N'*-bis(2-methylpyridyl)-ethylenediamine] (LMCT bands: 323 and 575 nm, $\Delta_o \approx$ 13 500 cm^{-1}).[44] For native human serum transferrin, the LMCT absorptions occur at 330 nm (shoulder) and 465 nm[41b] with an energy separation of ~8800 cm^{-1}; this relatively low value of Δ_o is in agreement with the comparatively low ligand field strength (FeNO$_5$ donor set; cf., FeN$_3$O$_3$/FeN$_4$O$_2$ donor sets for [Fe(bipy)(5,3-Cl,Me)-L], [Fe(EDDHA)]$^-$, and [Fe(bbpen)]$^+$).

Finally, the electronic effect of the phenolic substituent groups on the charge-transfer transitions is much more pronounced for the visible absorption as illustrated by the visible spectra of [Fe(bipy)(5,3-Cl,Me)-L]·MeCN (λ_{max} = 515 nm; ϵ = 3100 dm^3 mol^{-1} cm^{-1}) and [Fe(bipy)(3,5-Br$_2$)-L]·MeCN (λ_{max} = 492 nm; ϵ = 2900 dm^3 mol^{-1} cm^{-1}) [Figure 6c]. The electron-donating methyl group in the former complex facilitates the LMCT transition, thereby lowering its energy.[43b,45] The magnitude and significance of the difference in the energies of the visible absorptions for these two complexes are evidenced by the discernible color differences in methanol.[45]

Conclusion

The asymmetric coordination of the pyridyl nitrogen atoms of bipy to the high-spin Fe^{III} centers in the complexes [Fe(bipy)L]·MeCN is largely a consequence of the trans influence of one of the two phenolate oxygen atoms of the mixed-donor tripodal ligands, L^{3-}.[6i,l,13,21,30] Although elongation of bonds trans to the [V=O]$^{2+}$ bond in oxovanadium(IV) complexes[25a−d] is commonly observed, this phenomenon has not been encountered in iron(III)−bipy complexes previously. As might be expected, the coordination behaviors of bipy and phen in the current system of iron(III) compounds are virtually identical. The electronic transitions resulting from the interactions of the phenolate moieties with iron(III) impart intense colors to these ternary complexes.[6i,l,43,44] Studies of the quadridentate tripodal ligands as possible functional models for catechol dioxygenases are underway. As indicated previously,[13] nature makes use of the asymmetric binding of the substrate (such as 3,4-dihydroxybenzoate, PCA) to iron(III) in protocatechuate 3,4-dioxygenase (3,4-PCD) to activate the substrate for bond cleavage and oxygenation. This is a direct result of the strong trans influence of Tyr408 weakening the Fe−PCA^{O3} bond.[13,21]

Experimental Section

General Considerations. All starting materials were purchased from Aldrich and used as received. The ligands H$_3$(3,5-Br$_2$)-L and H$_3$(5,3-Cl,Me)-L were synthesized by the Mannich reaction following the procedure reported by Wilson[14] with minor modifications

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(45) Shongwe, M. S.; Al-Hatmi, S. K. M.; Marques, H. M.; Smith, R.; Nukada, R.; Mikuriya, M. *J. Chem. Soc., Dalton Trans.* **2002**, 4064.

to optimize the reaction conditions. Infrared spectra were recorded with the samples compressed as KBr disks on a Nicolet MAGNA 560 FTIR or a Nicolet Impact 400D FTIR spectrophotometer in the range 4000−400 cm^{-1}. Microanalyses were carried out at University College London. FAB mass spectra were measured with a VG AutoSpecQ mass spectrometer at Imperial College. UV−visible absorption spectra were recorded on a Varian Cary IE or an HP845 UV−visible spectrophotometer in the range 200−900 nm. Magnetic susceptibility measurements were carried out using an MPMS Quantum Design magnetometer in the range 300−5 K. X-band EPR spectra were recorded at 100−103 K on a Varian E-line or Varian E-104A spectrometer equipped with a variable-temperature accessory and operating at ∼9.0 GHz. The spectral *g* values were calibrated with (diphenylpicryl)hydrazyl (DPPH) as a standard.

Synthesis of [Fe(bipy)(3,5-Br$_2$)-L]·MeCN (1·MeCN). Et$_3$N (0.0304 g, 0.300 mmol) was added to a suspension of H$_3$(3,5-Br$_2$)-L (0.0603 g, 0.100 mmol) in a solvent mixture of MeOH/EtOH/MeCN (3:3:2; 8 cm^3) with continuous stirring, followed by Fe(NO$_3$)$_3$·9H$_2$O (0.0404 g, 0.100 mmol), upon which addition the mixture turned violet instantaneously. Thereafter, 2,2′-bipyridine (0.0156 g, 0.0999 mmol) was added, causing the color of the solution to darken somewhat. Within 5 min of gentle stirring, the resultant intense violet solution was filtered and allowed to evaporate slowly under controlled conditions at room temperature. [Note: Prolonged stirring of the final solution resulted in the formation of a precipitate, especially when Fe(ClO$_4$)$_3$·*x*H$_2$O was used as the source of Fe^{III}.] Rectangular blocks of red-purple crystals were obtained after several days. Yield: 0.0613 g (71.9%). $\Lambda_M = 3$ S cm^2 mol^{-1} (in DMF). Anal. Calcd for Br$_4$C$_{28}$H$_{21}$N$_4$O$_4$Fe: C, 39.43; H, 2.48; N, 6.57. Found: C, 39.39; H, 2.40; N, 6.41. FAB MS: *m*/*z* 812 (M$^+$), 767, 504, 213, 157, 89, 77.

Synthesis of [Fe(phen)(3,5-Br$_2$)-L]·MeCN (2·MeCN). This compound was synthesized following closely the procedure described for **1**·MeCN, but using 1,10-phenanthroline instead of 2,2′-bipyridine. The intense solution of **2**·MeCN afforded blocks of reddish-purple crystals on slow evaporation lasting several days. Yield: 0.0569 g (65.0%). $\Lambda_M = 4$ S cm^2 mol^{-1} (in DMF). Anal. Calcd for Br$_4$C$_{30}$H$_{21}$N$_4$O$_4$Fe: C, 41.09; H, 2.41; N, 6.39. Found: C, 41.01; H, 2.38; N, 6.33. FAB MS: *m*/*z* 836 (M$^+$), 791, 528, 237, 181, 89, 77.

Synthesis of [Fe(bipy)(5,3-Cl,Me)-L]·MeCN (3·MeCN). Likewise, this compound was synthesized using a procedure analogous to that described for **1**·MeCN, but substituting H$_3$(3,5-Br$_2$)-L with H$_3$(5,3-Cl,Me)-L. The resultant purple-violet solution of **3**·MeCN gave blocks of black-purple crystals on slow evaporation over several days. Yield: 0.0488 g (77.0%). $\Lambda_M = 6$ S cm^2 mol^{-1} (in DMF). Anal. Calcd for Cl$_2$C$_{30}$H$_{27}$N$_4$O$_4$Fe: C, 56.81; H, 4.29; N, 8.83. Found: C, 56.53; H, 4.24; N, 8.61. FAB MS: *m*/*z* 593 (M$^+$), 520, 394, 213, 157, 89, 77.

Crystal Structure Determinations. Single-crystal X-ray diffraction analyses were performed on a Bruker SMART CCD area detector diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data reduction was performed with the SAINT software,[46a] and absorption corrections were applied using the SADABS program.[46b] The structures of **1**·MeCN and **3**·MeCN were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXTL software package.[46c] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. The crystallographic data for **1**·MeCN and **3**·MeCN are summarized in Table 3.

Table 3. Selected Crystallographic Data for [Fe(bipy)(3,5-Br$_2$)-L]·MeCN (**1**·MeCN) and [Fe(bipy)(5,3-Cl,Me)-L]·MeCN (**3**·MeCN)

	1·MeCN	**3**·MeCN
empirical formula	C$_{28}$H$_{21}$Br$_4$FeN$_4$O$_4$	C$_{30}$H$_{27}$Cl$_2$FeN$_4$O$_4$
fw	852.98	634.31
T/K	293	293
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.7294(6)	10.8120(7)
b/Å	11.2504(6)	10.9511(7)
c/Å	12.9565(8)	12.8649(9)
α/deg	95.7760(10)	94.065(1)
β/deg	96.7920(10)	96.567(1)
γ/deg	104.7670(10)	104.550(1)
V/Å^3	1487.71(15)	1456.84(17)
Z	2	2
μ(Mo Kα)/mm^{-1}	5.920	0.744
collected reflections	8055	7859
independent reflections	5342	5202
R_{int}	0.0452	0.0196
R1 [$I > 2\sigma(I)$]	0.0576	0.0481
wR2 (all data)	0.1451	0.1137

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Note Added after ASAP Publication: This article was published ASAP on April 2, 2005, with minor text errors in the Magnetic Properties and Crystal Structure Determinations paragraphs. The Web version published on April 5, 2005, and the print version are correct.

Supporting Information Available: Crystallographic data for [Fe(bipy)(3,5-Br$_2$)-L]·MeCN and [Fe(bipy)(5,3-Cl,Me)-L]·MeCN in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) (a) Bruker. *SAINT+*, version 6.02 (includes XPREP and SADABS); Bruker AXS Inc.: Madison, WI, 1999. (b) Sheldrick, G. M. *SADABS*; University of Gottingen: Germany, 1996. (c) Bruker. *SHELXTL*, version 5.1 (includes XS, XL, XP, XSHELL); Bruker AXS Inc.: Madison, WI, 1999.