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Title: Iron(III) Complexes of a Hexadentate Thioether-Appended 2-Aminophenol Ligand: Redox-Driven Spin State Switchover

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Redox-Driven Spin State Switchover

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Abstract: A green complex [Fe(L3)] (1), supported by the deprotonated form of a hexadentate noninnocent redox-active thioether-appended 2-aminophenolate ligand (H4L3 = N,N'-bis(2-hydroxy-3,5-di-tert-butylphenyl)-2,2'-diaminodiphenyldithioethane), has been synthesized and structurally characterized at 100(2) K and 298(2) K. In CH₂Cl₂, 1 displays two oxidative and a reductive one-electron redox processes at E_{1/2} values of -0.52 and 0.20 V, and -0.85 V versus the Fc⁺/Fc redox couple, respectively. The one-electron oxidized 1⁺ and one-electron reduced 1⁻ forms, isolated as a blackish-blue solid 1(PF₆)·CH₂Cl₂ (2) and a gray solid [Co(η⁵-C₅H₅)₂]⁺·DMF (3), have been structurally characterized at 100(2) K. Structural parameters at 100 K of the ligand backbone and metrical oxidation state values unambiguously establish the electronic states as [FeIII{(LAPO,N)2-}{(LISQO,N)-}{(LS,S)0}}] (1) (two tridentate halves are electronically asymmetric-ligand mixed-valency), [FeIII{(LISQO,N)-}{(LISQO,N)-}{(LS,S)0}}] (1⁺), and [FeIII{(LAPO,N)2-}{(LAPO,N)2-}{(LS,S)0}}] (1⁻) [dianionic 2-aminophenolate(2-) (LAPO,N)2- and monoanionic 2-iminobenzosemiquinonate(1-) π-radical (S_{rad} = 1/2) (LISQ)- redox level]. Mössbauer spectral data of 1 at 295, 200, and 80 K reveal that it has a major low-spin (ls)-Fe(III) and a minor ls-Fe(II) component (redox isomers), and at 7 K, the major component exists exclusively. Thus, in 1, the occurrence of a thermally driven valence-tautomeric (VT) equilibrium (asymmetric) [FeIII{(LAPO,N)2-}{(LISQO,N)-}{(LS,S)0}}] ⇌ (symmetric) [FeII{(LISQO,N)-}{(LISQO,N)-}{(LS,S)0}}] (80–295 K) is implicated. Mössbauer spectral parameters unequivocally establish that 1⁺ is a ls-Fe(III) complex. In contrast, the monoanion 1⁻ contains a high-spin (hs)-Fe(III) center (S_{Fe} = 5/2), as is deduced from its Mössbauer and EPR spectra. Complexes 1–3 possess total spin ground states S_t = 0, 1/2, and 5/2, respectively, based on ¹H NMR and EPR spectra, the variable-temperature (2–300 K) magnetic behavior of 2, and the μ_{eff} value of 3 at 300 K. Broken-symmetry density functional theory (DFT) calculations at the B3LYP-level of theory reveal that the unpaired electron in 1⁺/2 is due to the (LISQ)- redox level [ls-Fe(III) (S_{Fe} = 1/2)] is strongly antiferromagnetically coupled to one of the (LISQ)- radicals (S_{rad} = 1/2), and 1⁻/3 is a hs-Fe(III) complex, supported by (L3)4- with two-halves in the (LAP)2- redox level. Complex 1 can have either a symmetric or asymmetric electronic state. As per DFT calculation, the former state is stabilized by -3.9 kcal/mol over the latter (DFT usually stabilizes electronically symmetric structure). Time-dependent (TD)-DFT calculations shed light on the origin of observed UV-vis-NIR spectral absorptions for 1–3 and corroborate the results of spectroelectrochemical experiments (300–1100 nm) on 1 (CH₂Cl₂; 298 K). Variable-temperature (218–298 K; CH₂Cl₂) absorption spectral (400–1000 nm) studies on 1 justify the presence of VT equilibrium in the solution-state.

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