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Communication

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Unsymmetrical Bimetallic Complexes with M^{II}–(μ-OH)–M^{III} Cores ($M^{II}M^{III}$ = $Fe^{II}Fe^{III}$, $Mn^{II}Fe^{III}$, $Mn^{II}Mn^{III}$): Structural, Magnetic, and Redox Properties

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Supporting Information

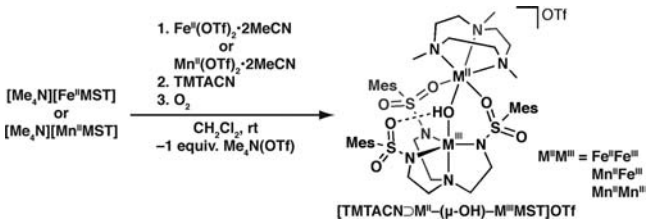
ABSTRACT: Heterobimetallic cores are important units within the active sites of metalloproteins but are often difficult to duplicate in synthetic systems. We have developed a synthetic approach for the preparation of a complex with a Mn^{II}–(μ-OH)–Fe^{III} core, in which the metal centers have different coordination environments. Structural and physical data support the assignment of this complex as a heterobimetallic system. A comparison with analogous homobimetallic complexes, Mn^{II}–(μ-OH)–Mn^{III} and Fe^{II}–(μ-OH)–Fe^{III} cores, further supports this assignment.

Transition-metal complexes with discrete dinuclear metal cores have important functional consequences in chemical and biological systems. In biology, several examples have been discovered in which both homo- and heterobimetallic centers are present within the active sites of proteins. Many metalloproteins, such as methanemonoxygenase hydroxylase, hemerythrin, purple acid phosphatases, and ribonucleotide reductases (RNRs), utilize oxo- or hydroxo-bridged homobimetallic cores that contain Fe or Mn ions.[1] More recently, several classes of RNRs have been found to contain heterobimetallic MnFe cores.[2] These enzymes catalyze the reduction of nucleotides to 2′-deoxynucleotides via the activation of dioxygen or hydrogen peroxide and are known to play an essential role in nucleic acid metabolism.[3] The function of most bimetallic active sites in metalloproteins often requires intermediates that contain an open coordination site for binding and activating small molecules.[4]

A variety of $M^{II}M^{III}$ bimetallic synthetic complexes that contain a bridging hydroxo or phenoxo group have been described previously. In many instances, these complexes utilize symmetric dinucleating ligands[5−7] or form coordinatively saturated geometries around each metal center.[8,9] We reported recently that the tetradentate sulfonamide-based tripodal ligand *N*,*N*′,*N*″-[2,2′,2″- nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) ($[MST]^{3-}$) enforces a five-coordinate geometry around a transition-metal center and contains a second metal-ion binding site to form heterobimetallic systems. Using this ligand, complexes with [M^{II}–(μ-OH)–M^{III}] cores (M^{II} = Ca, Sr, Ba; M^{III} = Mn, Fe) were prepared from the activation of dioxygen.[10] We have expanded the scope of our heterobimetallic systems to include two 3d transition-metal ions (Fe and Mn) in which the metal centers are linked through a bridging hydroxo ligand and two sulfonamide groups of the $[M^{III}(OH)MST]^-$ complex. The primary coordination sphere of the second metal ion is completed by 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN) to form a six-coordinate metal center.

The preparation of $[TMTACN⊃Mn^{II}–(\mu\text{-}OH)–Fe^{III}MST]^+$ (denoted as $[Mn^{II}(OH)Fe^{III}]^+$) was achieved via the synthetic route outlined in Scheme 1. The visible absorbance spectrum of

Scheme 1. Preparative Route to $[TMTACN⊃M^{II}–(\mu\text{-}OH)–M^{III}MST]^-$ Complexes



the isolated solid showed an absorbance band at λ_{max} (ε_M) = 390 nm (4600) and a broad shoulder at 470 nm (1780 M) (Figure S1 in the Supporting Information, SI). A broad but intense band was observed in the Fourier transform infrared (FTIR) spectrum at 3244 cm^{-1}, which was assigned to the vibration of the O–H bond (Figure S2 in the SI).[10] The broadness of this band suggests a strong intramolecular hydrogen bond between the hydroxo ligand and sulfonamide group. The formulation of the solid as $[Mn^{II}(OH)Fe^{III}]^+$ was supported by electrospray ionization mass spectrometry (ESI-MS), in which the molecular weight and experimental isotope pattern matched those calculated for $[Mn^{II}(OH)Fe^{III}]^+$ (Figure S3 in the SI). Using the same synthetic route, $[TMTACN⊃Fe^{II}–(\mu\text{-}OH)–Fe^{III}MST]^+$ ($[Fe^{II}(OH)Fe^{III}]^+$) and $[TMTACN⊃Mn^{II}–(\mu\text{-}OH)–Mn^{III}MST]^+$ ($[Mn^{II}(OH)Mn^{III}]^+$) were also prepared and characterized. These homobimetallic complexes served as control systems for $[Mn^{II}(OH)Fe^{III}]^+$ and possessed properties expected for their formulation. For example, their ESI-MS spectra were consistent with those for homobimetallic complexes (Figure S3 in the SI). In addition, $[Fe^{II}(OH)Fe^{III}]^+$ had an absorbance spectrum similar to that for $[Mn^{II}(OH)Fe^{III}]^+$ with a peak at λ_{max} = 387 nm (6200), which appears to be representative

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of complexes containing $[Fe^{III}(OH)MST]^-$ units (Figure S1 in the SI).

The molecular structure of $[Mn^{II}(OH)Fe^{III}]^+$ was determined by X-ray diffraction methods and revealed the expected heterobimetallic complex (Figure 1). The Fe^{III} and Mn^{II} centers

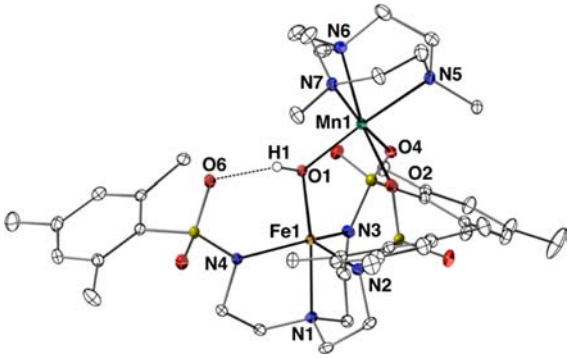

Figure 1. Thermal ellipsoid diagram depicting the molecular structure of $[Mn^{II}(OH)Fe^{III}]^+$. Ellipsoids are drawn at the 50% probability level, and only the hydroxo H atom is shown for clarity. Selected bond lengths (Å): Fe1−O1, 1.888(1); Fe1−N1, 2.193(2); Fe1−N2, 2.030(2); Fe1−N3, 2.007(2); Fe1−N4, 2.036(2); Fe1···Mn1, 3.447(1); Mn1−O1, 2.048(1); Mn1−N5, 2.268(2); Mn1−N6, 2.276(2); Mn1−N7, 2.294(2); Mn1−O2, 2.196(1); Mn1−O4, 2.187(1); O1···O6, 2.646(2).

have different coordination geometries: the Fe^{III} center exhibits a five-coordinate, N_4O primary coordination sphere with a distorted trigonal-bipyramidal geometry. In contrast, the Mn^{II} center has a six-coordinate, N_3O_3 primary coordination sphere with a distorted octahedral geometry (Table S4 in the SI). Note that the configuration of the SO_2Ar groups produced a cavity that forms an intramolecular hydrogen bond between the Fe^{III}−OH−Mn^{II} unit and O6 of the $[MST]^{3-}$ ligand with an O1···O6 distance of 2.646(2) Å. The molecular structures of the homobimetallic complexes $[Fe^{II}(OH)Fe^{III}]^+$ and $[Mn^{II}(OH)Mn^{III}]^+$ were also determined (Figures S4 and S5 in the SI) and used to support the assignment of $[Mn^{II}(OH)Fe^{III}]^+$ as a heterobimetallic species (Table S4 in the SI). For instance, for the M^{II} center, the average M^{II}−N_{TMTACN} bond distance is statistically the same in $[Mn^{II}(OH)Mn^{III}]^+$ as it is in $[Mn^{II}(OH)Fe^{III}]^+$ [2.277(7) vs 2.279(2) Å]; both values are significantly longer than the average bond distance of 2.210(2) Å observed in $[Fe^{II}(OH)Fe^{III}]^+$. Moreover, the displacements of the M^{II} center from the plane formed by N5, N6, and N7 in $[Mn^{II}(OH)Mn^{III}]^+$ and $[Mn^{II}(OH)Fe^{III}]^+$ are nearly identical (1.557 vs 1.552 Å), while that found in $[Fe^{II}(OH)Fe^{III}]^+$ is 1.471 Å. For the M^{III} center, the displacements of the M^{III} center from the plane formed by N2, N3, and N4 of $[MST]^{3-}$ are 0.359 Å in $[Mn^{II}(OH)Fe^{III}]^+$ and 0.356 Å in $[Fe^{II}(OH)Fe^{III}]^+$, yet in $[Mn^{II}(OH)Mn^{III}]^+$, this displacement is only 0.286 Å.

Electron paramagnetic resonance (EPR) spectroscopy was used to further probe the properties of these complexes. For $[Mn^{II}(OH)Mn^{III}]^+$, the EPR spectrum measured at 11 K displayed a signal from an $S = {}^1/_2$ spin ground state of antiferromagnetically coupled Mn^{II} and Mn^{III} high-spin centers (Figure 2A). This signal displays an irregular pattern of hyperfine lines from the inequivalent nuclear spins of the two Mn centers. For $[Fe^{II}(OH)Fe^{III}]^+$, the EPR spectrum measured at 11 K displayed a rhombic signal with g values of 1.91, 1.68, and 1.54 (Figure 2B). This type of spectrum is characteristic of complexes with an antiferromagnetically coupled Fe^{II}−(μ-OH)−Fe^{III} core.[5a] For both complexes, spin quantification of the spectra

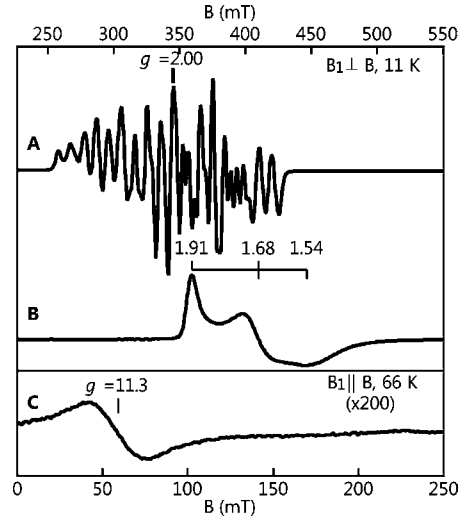

Figure 2. X-band EPR spectra for (A) $[Mn^{II}(OH)Mn^{III}]^+$, (B) $[Fe^{II}(OH)Fe^{III}]^+$, and (C) $[Mn^{II}(OH)Fe^{III}]^+$.

indicated that the signals accounted for the amount of metal used in the reaction. No EPR signals were observed for $[Mn^{II}(OH)Fe^{III}]^+$ at a temperature of 4 K. However, at higher temperatures (e.g., 66 K), a signal is observed at g = 11.3 for the microwave magnetic field oscillating parallel to the static magnetic field (Figure 2C). The absence of signals at low temperature and the presence of the parallel-mode signal at higher temperatures is consistent with antiferromagnetic coupling between the two d^5 metal centers in $[Mn^{II}(OH)Fe^{III}]^+$. The observed antiferromagnetic coupling between the two metal centers is a key result that supports the persistence of the bimetallic complexes in solution.

The electrochemical results further support that the $[M^{II}(OH)M^{III}]$ complexes are assembled in solution. The cyclic voltammogram for each complex exhibits two quasi-reversible one-electron redox processes that are assigned to the $M^{II}M^{II}$/$M^{II}M^{III}$ and $M^{II}M^{III}$/$M^{III}M^{III}$ couples (Figure 3). The most striking finding is that the two redox processes observed for the $[Mn^{II}(OH)Fe^{III}]^+$ complex are nearly identical with the analogous redox process in the $[Fe^{II}(OH)Fe^{III}]^+$ and $[Mn^{II}(OH)Mn^{III}]^+$ complexes. Specifically, the $Mn^{II}Fe^{II}$/$Mn^{II}Fe^{III}$ couple at −0.88 V matches the $Fe^{II}Fe^{II}$/$Fe^{II}Fe^{III}$ couple

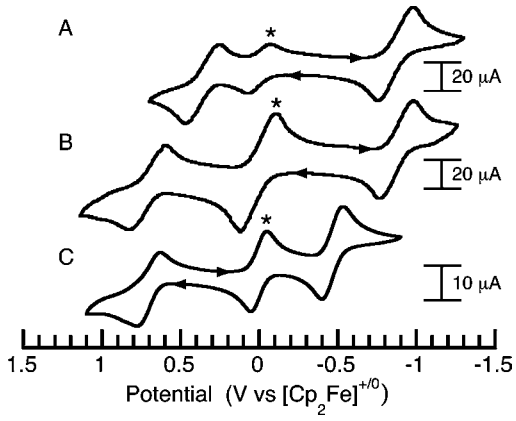

Figure 3. Cyclic voltammograms of (A) $[Fe^{II}(OH)Fe^{III}]^+$, (B) $[Mn^{II}(OH)Fe^{III}]^+$, and (C) $[Mn^{II}(OH)Mn^{III}]^+$ measured in CH_2Cl_2 (0.1 M TBAP). The cyclic voltammograms in parts A and B were collected at 100 mV s^{-1} and that in part C at 20 mV s^{-1} in the presence of $[Cp_2Fe]$ (*).

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at −0.87 V, while the $Mn^{II}Fe^{III}/Mn^{III}Fe^{III}$ couple at 0.71 V matches the $Mn^{II}Mn^{III}/Mn^{III}Mn^{III}$ couple at 0.71 V. These results indicate that the Mn^{II} ion resides in the [TMTACN] binding site and the Fe^{III} center is coordinated to the $[MST]^{3-}$ ligand. Furthermore, the separations between the first and second redox processes in the $[M^{II}(OH)M^{III}]^{+}$ systems are extremely large, with differences of 1.59, 1.23, and 1.18 V for the $[Mn^{II}(OH)Fe^{III}]^{+}$, $[Fe^{II}(OH)Fe^{III}]^{+}$, and $[Mn^{II}(OH)Mn^{III}]^{+}$ complexes. These separations suggest that the mixed-valence $[M^{II}(OH)M^{III}]^{+}$ species should be relatively stable toward disproportionation.[5−8]

In summary, we have described the preparation and properties of a series of hetero- and homobimetallic complexes of Fe and Mn ions in differing coordination environments. Structural studies confirmed that each complex contains a $M^{II}-(\mu\text{-}OH)-M^{III}$ core, with the hydroxo ligand also forming an intramolecular hydrogen bond with the $[MST]^{3-}$ ligand. The metal-ion cores adopt stable mixed-valent states of $Mn^{II}Fe^{III}$, $Fe^{II}Fe^{III}$, and $Mn^{II}Mn^{III}$, whose assignments are supported by EPR results that are consistent with antiferromagnetic coupling of the spins through the hydroxo unit. In addition, two quasi-reversible one-electron redox processes corresponding to the $M^{II}M^{II}/M^{II}M^{III}$ and $M^{II}M^{III}/M^{III}M^{III}$ couples were clearly observed with all of the $[M^{II}(OH)M^{III}]^{+}$ systems via cyclic voltammetry. These results further illustrate the ability of tripodal sulfonamido ligands to form discrete bimetallic complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, experimental details, and UV−vis, FTIR, and ESI-MS spectra for all complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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