Tris(chloranilato)ferrate(III) Anionic Building Block Containing the (Dihydroxo)oxodiiron(III) Dimer Cation: Synthesis and Characterization of [(TPA)(OH)Fe^{III}OFe^{III}(OH)(TPA)][Fe(CA)$_3$]$_{0.5}$(BF$_4$)$_{0.5}$·1.5MeOH·H$_2$O [TPA = tris(2-pyridylmethyl)amine; CA = chloranilate]

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Metal compounds with 1,4-dihydroxybenzoquinonediide, chloranilate (CA^{2-}) ligands display interesting redox chemistry as they have a delocalized π system and can coordinate in either a bidentate or bis-bidentate manner.[1] These studies, however, have been limited to homometallic multinuclear compounds[1,2] and 1- or 2-D polymers,[1,3] as [M^{III}(CA)$_3$]$^{3-}$ have yet to be reported. The related [M(ox)$_3$]$^{3-}$ (M = V, Cr, Fe; ox = oxalato) have been used to form magnetically ordered heterobimetallic 2-D layered materials.[4] Herein, we report the formation of [Fe^{III}(CA)$_3$]$^{3-}$ and, in an atom economical synthesis, a (dihydroxo)oxodiiron(III) dimer [(TPA)-(OH)Fe^{III}O-Fe^{III}(OH)(TPA)]$^{2+}$ (TPA = tris(2-pyridylmethyl)amine) cation. The anion is a building block for making new redox-active and molecule-based magnets, and the cation is a bioinorganic model compound for metalloenzymes, such as methane monooxygenase, ribonucleotide reductase, and purple acid phosphatases.[5]

[(TPA)(OH)Fe^{III}OFe^{III}(OH)(TPA)][Fe(CA)$_3$]$_{0.5}$(BF$_4$)$_{0.5}$·1.5MeOH·H$_2$O (**1**) was synthesized as follows. A MeOH solution (15 mL) of Fe(BF$_4$)$_2$·6H$_2$O (116 mg, 0.344 mmol) was added to a MeOH solution (7 mL) of tris(2-pyridylmethyl)amine (TPA, 100 mg, 0.344 mmol) and a MeOH solution (10 mL) of chloranilic acid (H$_2$CA, 36 mg, 0.172 mmol). The color turned dark green and formed a dark brown solid. Triethylamine (0.05 mL, 0.344 mmol) was added to the mixture for neutralization, which gives rise to a clear reddish-brown solution that was heated to reflux for 30 min. After a hot-filtration, the solution was allowed to stand at room temperature for 2 or 3 days, whereupon dark reddish-brown crystals formed which were collected by filtration and washed with methanol and dried in air (yield: 110 mg, 66%).[6]

Red-brown block-shaped crystals of **1** suitable for X-ray crystal analysis were obtained by allowing the reaction mixture to stand for several days without agitation. Compound **1** crystallizes in the monoclinic $C2/c$ space group, and the ORTEP drawing of **1** is shown in Figure 1.[7] The core structure of **1** is composed of two (dihydroxo)oxodiiron(III) dimer dications, the tris(chloranilate)-ferrate(III) trianion as well as a [BF$_4$]$^-$. The structure of **1** shows an almost linear (dihydroxo)oxodiiron(III) core, with an Fe−O−Fe angle of 158.06(15)° and an Fe−Fe distance of 3.503(3) Å. The main structural parameters are consistent with those found for other monobridged (μ-oxo)diiron(III) complexes.[8] Each Fe(III) ion is coordinated to a TPA, with the amine nitrogen *trans* to the oxo ligand, as is found in [(TPA)(H$_2$O)FeOFe(OH)(TPA)](ClO$_4$)$_3$.[8d] Interestingly, both Fe(III) ions (Fe2 and Fe3) have a hydroxide ion as the sixth ligand, with Fe−O distances of 1.880(2) and 1.885(2) Å, respectively. These Fe−O$_{OH}$ bond distances are comparable to those reported for [(TPA)(H$_2$O)FeOFe(OH)(TPA)](ClO$_4$)$_3$ and [(5-Et-TPA)(H$_2$O)FeOFe(OH)(5-Et-TPA)](ClO$_4$)$_3$.[8d,e] To date, many oxoiron(III) dimers are reported; however, to the best of our knowledge, this is the first example of (dihydroxo)oxodiiron(III).
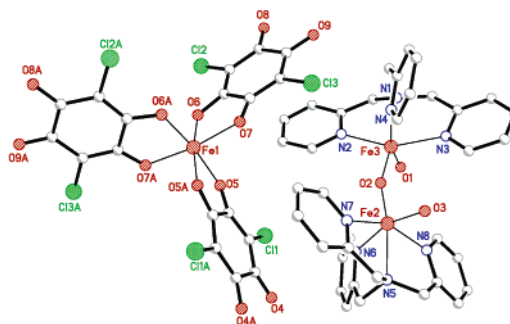

Figure 1. ORTEP view of **1**. The atoms are represented by 50% probable thermal ellipsoids. Hydrogen atoms, solvent, and [BF$_4$]$^-$ are omitted for clarity. Relevant distances (Å) and angles (°): Fe1−O5 2.010(2), Fe1−O6 1.978(2), Fe1−O7 2.012(3), Fe2−N5 2.244(3), Fe2−N6 2.169(3), Fe2−N7 2.141(3), Fe2−N8 2.150(3), Fe3−N1 2.231(3), Fe3−N2 2.143(3), Fe3−N3 2.171(3), Fe3−N4 2.166(3), Fe2−O2 1.781(2), Fe2−O3 1.885(2), Fe3−O2 1.788(2), Fe3−O1 1.880(2), O6−Fe1−O7 80.93(9), Fe2−O2−Fe3 158.06(15), N1−Fe3−O2 168.64(11), N5−Fe2−O2 169.91(10).
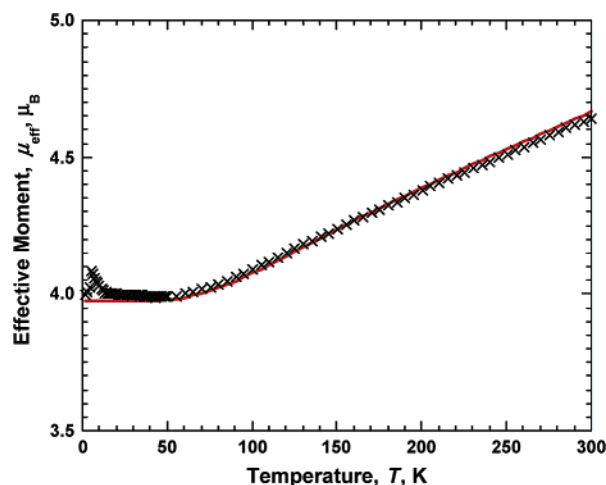

Figure 2. $\mu_{eff}(T)$ for **1** taken at 300 Oe. The solid line is the best fit curve to eq 1.

This cation may be used for the characterization of catalytic properties of metalloenzymes as a model compound.

The unprecedented [Fe(CA)$_3$]$^{3-}$ unexpectedly formed (Figure 1). The Fe(III) ion is coordinated with six oxygen atoms of three chloranilate dianions as trigonally distorted octahedron, with approximate D_3 symmetry. This basic motif is very similar to [M(ox)$_3$]$^{3-}$ complexes (M = Fe, Cr, V).[4] The Fe−O$_{CA}$ distances range from 1.978(2) to 2.012(3) Å and average 1.997(1) Å. The average ligand bite distances of the coordinated (O6···O7 and O5···O5A) five-membered chelate ring and noncoordinated

(O8···O9 and O4···O4A) oxygens are 2.589(3) and 2.688(3) Å, respectively. The former is identical to 2.585 Å observed for $[Fe(ox)_3]^{3-}$;[9] however, the latter is shorter than the $[Fe(ox)_3]^{3-}$s, 2.772 Å.

Variable-temperature 2−300 K magnetic susceptibility, χ, measurements on a solid sample of **1** have been performed on a SQUID magnetometer. At room temperature, the effective moment, $\mu_{eff} = (8\chi T)^{1/2}$, is 2.93 μ_B/Fe, and $\mu_{eff}(T)$ decreases with decreasing temperature until it reaches a plateau at ca. 55 K, indicating a strong antiferromagnetic interaction within the $Fe^{III}OFe^{III}$ unit. Below 55 K, $\chi(T)$ is constant at 4.00 μ_B, which is attributed solely to $[Fe(CA)_3]^{3-}$. The $\chi(T)$ data were fit to an analytical expression for a coupled $S = 5/2$ dimer and an $S = 5/2$ Curie−Weiss term for the uncoupled $[Fe(CA)_3]^{3-}$, eq 1 ($H = -2J\mathbf{S}_a\cdot\mathbf{S}_b$). The best fit had J/k_B of −165 K (115 cm^{-1}), $g = 2.07$, $\theta = -1$ K, and the spin impurity $\rho = 0.05$.[10]

$$\chi = \{Ng^2\mu_B^2/k(T-\theta)\}F(T)(1-\rho) + 2\rho(Ng^2\mu_B^2/3kT)S_1(S_1+1) + (Ng^2\mu_B^2/3kT)S_2(S_2+1) \quad (1)$$

where $S_1 = 5/2$, $S_2 = 5/4$, and $F(T) = \{2\exp(2J/kT) + 10\exp(6J/kT) + 28\exp(12J/kT) + 60\exp(20J/kT) + 110\exp(30J/kT)\}/\{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT) + 9\exp(20J/kT) + 11\exp(30J/kT)\}$.

This experimentally determined J value for **1** is on the higher side, but is in the range observed for other oxo-bridged Fe(III) complexes with TPA as capping ligand, that is, $J = -107 \pm 10$ cm^{-1}.[8d]

In conclusion, we have simultaneously synthesized both $[Fe^{III}(CA)_3]^{3-}$ and a new (dihydroxo)oxodiiron(III) dimer. Further studies on the separate isolation of each ion, as well as their reactivity, and preparation of new layered magnetic materials are ongoing.

Supporting Information Available: Tables of the structure of **1**. An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Characterization of **1**: Absorption spectrum (MeCN), λ_{max}, nm (ϵ_M, L mol^{-1} cm^{-1}): 312 (1.3 × 10^4), 356 (1.6 × 10^4), 512 (3.4 × 10^3). IR (KBr): ν_{CH} 3069 (w), 2920 (w), 1643 (m), 1607 (s), 1528 (vs), 1445 (s), 1352 (vs), 1304 (s), 1052 (multiple, br), 842 (vs), 772 (s), 597 (m), 574 (m), 505 (m) cm^{-1}. Anal. Calcd for $C_{46.5}H_{46}B_{0.5}Cl_3F_2Fe_{2.5}N_8O_{11.5}$: C, 46.92; H, 3.90; N, 9.41. Found: C, 46.57; H, 3.66; N, 9.24. This compound is air stable.
(7) Crystal and structure refinement parameters for **1**: $C_{46.5}H_{46}B_{0.5}Cl_3F_2Fe_{2.5}N_8O_{11.5}$, fw = 1190.28 g/mol, monoclinic, space group $C2/c$, $a = 37.026(16)$ Å, $b = 14.541(6)$ Å, $c = 19.374(9)$ Å, $\beta = 105.100(7)°$, $V = 10071(8)$ Å^3, $Z = 8$, $d_{calcd} = 1.570$ g/cm^3, μ(Mo Kα) = 0.950 mm^{-1}, $R1 = 0.0608$, $wR2 = 0.1449$. Data were collected on a Bruker SMART automatic diffractometer using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Structure was solved by direct methods and refined by full-matrix least-squares refinement using the SHELXL97 programs.
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(10) The data were corrected for diamagnetic contribution.

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