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Mixed Valency in a 3D Semiconducting Iron–Fluoranilate Coordination Polymer

Ryuichi Murase,^{†,‡} Brendan F. Abrahams,^{*,†} Deanna M. D'Alessandro,^{*,‡} Casey G. Davies,[§] Timothy A. Hudson,[†] Guy N. L. Jameson,^{§, \triangle} Boujemaa Moubaraki,[⊥] Keith S. Murray,[⊥] Richard Robson,^{*,†} and Ashley L. Sutton[†]

[†]School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia

[‡]School of Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia

[§]Department of Chemistry & MacDiarmid Institute for Advanced Materials & Nanotechnology, University of Otago, Dunedin, PO Box 56, New Zealand 9054

[⊥]School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

S Supporting Information

ABSTRACT: A pair of coordination polymers of composition $(NBu_4)_2[M_2(fan)_3]$ (fan = fluoranilate; M = Fe and Zn) were synthesized and structurally characterized. In each case the compound consists of a pair of interpenetrating three-dimensional, (10,3)-*a* networks in which metal centers are linked by chelating/bridging fluoranilate ligands. Tetrabuty-lammonium cations are located in the spaces between the two networks. Despite the structural similarity, significant differences exist between $(NBu_4)_2[Fe_2(fan)_3]$ and $(NBu_4)_2[Zn_2(fan)_3]$ with respect to the oxidation states of the metal centers and ligands. For $(NBu_4)_2[Fe_2(fan)_3]$ the structure determination as well as Mössbauer spectroscopy indicate the oxidation state for the Fe is close to +3, which contrasts with the +2 state for the Zn analogue. The differences between the two compounds extends to the ligands, with the Zn network involving only fluoranilate dianions,



whereas the average oxidation state for the fluoranilate in the Fe network lies somewhere between -2 and -3. Magnetic studies on the Fe compound indicate short-range ordering. Electrochemical and spectro-electrochemical investigations indicate that the fluoranilate ligand is redox-active in both complexes; a reduced form of $(NBu_4)_2[Fe_2(fan)_3]$ was generated by chemical reduction. Conductivity measurements indicate that $(NBu_4)_2[Fe_2(fan)_3]$ is a semiconductor, which is attributed to the mixed valency of the fluoranilate ligands.

INTRODUCTION

Coordination polymers, otherwise known as metal–organic frameworks (MOFs), have been recognized as versatile materials for a broad range of potential applications.¹ The tunability and rational design of the components allow for the construction of tailor-made porous materials that have found uses in gas sorption and separation, heterogeneous catalysis, and molecular sensing, among others. While there has been a strong emphasis on exploiting the host properties of porous coordination polymers there has also been interest in exploring the electrical and magnetic properties of coordination networks. For example, in recent years enormous strides have been made toward the realization of electrically conductive framework materials.^{2–7}

The dianion of 2,5-dihydroxy-1,4-benzoquinone (dhbq²⁻ X = H; I) and related species have been used extensively, in their dianionic form, to link metal centers within coordination polymers.⁸ The ability of these anionic, chelating ligands to bridge metal centers has led to robust two-dimensional (2D) and three-dimensional (3D) networks in which a wide variety

of metal centers can serve as nodes. In addition to their structural role, a particularly attractive feature of these ligands is their ability to exist in different redox states. The dianion is able to undergo a one-electron reduction to form a radical trianion (II) and a second one-electron reduction to form the aromatic tetraanion (III). In 2011 a synthetic and structural investigation of 3D networks of composition $(NBu_4)_2[M_2(dhbq)_3]$ (M = Mn, Fe, Co, Ni, Zn, and Cd) and (NBu₄)₂[Mn₂(can)₃] was reported $(can^{2-} = the dianion of 3,6-dichloro-2,5-dihydroxy-$ 1,4-benzoquinone; I, X = Cl).⁹ In this work the prospect of creating networks that employ bridging ligands and metal centers that are both amenable to facile electron transfer was discussed. This work was followed in 2012 by a report on a crystalline material of composition (PMePh₃)₂[Cd₂(dhbq)₃] that was able to undergo repeated cycles of electrochemical reduction and oxidation.¹⁰

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In 2015, Long and co-workers described investigations of the aforementioned $(NBu_4)_2$ [Fe₂(dhbq)₃], which indicated that, unlike $(NBu_4)_2[M_2(dhbq)_3]$ (M = Mn, Co, Ni, Zn, and Cd), the metal centers exist in the +3 oxidation state, according to Mössbauer spectroscopy.¹¹ A corollary of this is that two-thirds of the dhbg ligands exist formally as the radical trianion. From a crystallographic perspective, all dhbq ligands are identical, and thus the average charge on a dhbq ligand is -2.67. A broad absorption band in the range of 4000 to 14000 cm⁻¹ was attributed to intervalence charge transfer (IVCT) associated with the dhbq $^{2-/3-}$ bridging ligands. The through-bond mixed valency due to $dhbq^{2-/3-}$ ligand-based IVCT leads to one of the highest levels of intrinsic conductivity observed in a 3D coordination polymer $(0.16(1) \text{ S cm}^{-1})$. Also in 2015, Harris et al.¹² identified a +3 oxidation state for the Fe centers within a 2D hexagonal network material of composition $(Me_2NH_2)_2$ [Fe₂(can)₃]·2H₂O·6DMF (DMF = dimethylformamide). In this case the chloranilate anion may be considered to have an average oxidation state of -2.67. This work was followed by a paper, appearing in early 2017, that indicates that the compound and its desolvated form exhibits electrical conductivity of $1.4(7) \times 10^{-2}$ and $1.0(3) \times 10^{-2}$ S cm^{-1.1} Harris and co-workers also demonstrated that the compound can undergo reduction to form a compound in which all ligands are reduced to the -3 radical form, while the Fe retains its +3oxidation state. This compound forms a magnetically ordered phase below $T_c = 105$ K.

In 2016 Stock et al. reported compounds of composition $(NH_2Me_2)_3[Al_4(dhbq)_6]$ and $(NH_2Me_2)_3[Al_4(can)_6]$, which each had a similar 2D network to that reported by Harris et al. but with the bridging/chelating ligands linking Al(III) centers. In each of the structures reported by Stock, the ligands (dhbq or can) have an average charge of -2.5.¹⁴

We recently published a synthetic, structural, and spectroscopic investigation of a series of structurally related compounds of composition $(NEt_4)_2[M_2(can)_3]$ (M = Mg, Mn, Fe, Co, Ni, Cu, and Zn) and $(NEt_4)_2[Zn_2(fan)_3]$, (H₂fan = 3,6-difluoro-2,5-dihydroxy-1,4-benzoquinone, fluoranilic acid).¹⁵ Hexagonal anionic networks similar to those identified by Harris were found for this series; however, the tetraethylammonium cation plays a different structural role to the dimethylammonium cation in Harris's $(Me_2NH_2)_2[Fe_2(can)_3]$.^{12,13} In all cases except for the Fe compound, divalent metal ions are linked by either can²⁻ or fan²⁻. Bond valence sum calculations in addition to near-infrared spectra suggest that the Fe in $(NEt_4)_2[Fe_2(can)_3]$ is in the +3 oxidation state, while the chloranilate anion has an oxidation state intermediate between -2 and -3.

Our current interest lies with further exploration of the fluorinated form of H_2 dhbq, H_2 fan, which we have used with the intention of incorporating the fluoranilate anion into framework materials. The choice of fluoranilate as bis-bidentate "linkers" stems from the rationale that the electron-withdrawing effect of the fluoro substituents is expected to impact upon the redox activity of the resulting network. Herein, we report the

synthesis of two coordination polymers of composition $(NBu_4)_2[M_2(fan)_3]$ (M = Fe (1), Zn (2)). The characterization of 1 and 2 is supported by investigations of the electronic, magnetic, spectro-electrochemical (SEC) and optical properties.

EXPERIMENTAL SECTION

General Synthetic Details. The compound 2,3,5,6-tetrafluoro-1,4-benzoquinone was purchased from Sigma-Aldrich and used without further purification. FeCl₂·4H₂O (FSE), Zn(NO₃)₂·6H₂O (Mallinckrodt), and tetrabutylammonium bromide (Aldrich) were used without further purification. 2,5-Difluoro-3,6-dihydroxy-1,4benzoquinone dihydrate was synthesized according to a modified literature procedure.¹⁶ Lithium naphthalenide (0.1 M) in tetrahydrofuran (THF) was prepared using a modified reported procedure. The preparation of $Li_{0.27}$ {(NBu₄)₂[Fe₂(fan)₃]} was performed in an argon-filled glovebox. Characterization of compounds was performed under ambient conditions in air unless otherwise stated. Tetrahydrofuran was obtained from a PuraSolv solvent purification system and kept under an argon atmosphere. Solution-state ¹³C{1H} NMR spectra were recorded on a Bruker AVANCE 300 spectrometer operating at 75 MHz for ¹³C. ¹³C NMR chemical shifts were referenced internally to residual solvent resonances. Deuterated solvents were obtained from Cambridge Stable Isotopes and used as received. Microanalyses were performed at the Chemical Analysis Facility-Elemental Analysis Service in the Department of Chemistry and Biomolecular Science at Macquarie University, Australia. Inductively coupled plasma-optical emission spectrometer (ICP-OES) analysis was performed at the Mark Wainwright Analytical Center at the University of New South Wales, Australia.

Synthesis of 2,5-Difluoro-3,6-dihydroxy-1,4-benzoquinone-Dihydrate. 2,3,5,6-Tetrafluoro-1,4-benzoquinone (2.0 g, 0.11 mol) was dissolved in 25 mL of 1,4-dioxane. NaOH (8 M, 30 mL) was added slowly using a pipet while stirring. The dark brown solution was allowed to stir for 3 h at room temperature. A brown precipitate of Na₂fan was isolated by filtration and air-dried. 2,5-Difluoro-3,6-dihydroxy-1,4-benzoquinone was synthesized by the acidification of Na₂fan. Na₂fan (2.00 g, 9.01 mmol) was stirred in HCl (37%, 5 mL), whereupon precipitates of H₂fan, NaF, and NaCl were collected subsequently. H₂fan·2H₂O was recrystallized from acetone as red blocklike crystals (Yield: 0.71 g, 30.1%), IR: 3452, 2363, 2340, 1640, 1553, 737 cm⁻¹. ¹³C NMR (CD₃CN, 300 MHz) δ (ppm) 142.51, 139.05. Anal. Calcd for C₆H₂O₆F₂·2.5H₂O: C, 32.59%; H, 3.19%; N, 0%; found: C, 32.57%; H, 3.15%; N, <0.05%.

Synthesis of (NBu₄)₂[Fe₂(fan)₃] (1). A solution of Fe^{II}Cl₂·4H₂O (0.1 mmol), NBu₄Br (0.4 mmol), and LiOAc (0.4 mmol) in 3 mL of H₂O was allowed to diffuse into a solution of H₂fan (0.15 mmol) in 4 mL of acetone with a 1:1 H₂O-acetone buffer solution under ambient conditions in air. Dark purple tetrahedral crystals suitable for X-ray diffraction appeared within 4 d (Yield: 17.2 mg, 30.2%). IR (ATR): 2963 (w), 2876 (w), 1656 (w), 1537 (s), 1486 (m), 1347 (s), 1152 (w), 1087 (w), 997 (s) cm⁻¹. Anal. Calcd for Fe₂C₅₀H₇₂N₂O₁₂F₆. 7H₂O: C, 48.24%; H, 6.96%; N, 2.25%. Found: C, 48.15%; H, 5.95%; N, 2.21%.

Synthesis of (NBu₄)₂[Zn₂(fan)₃] (2). A solution of $Zn(NO_3)_2$. 6H₂O (30 mg, 0.1 mmol), NBu₄Br (65 mg, 0.2 mmol), and LiOAc (13 mg, 0.2 mmol) in 3 mL of H₂O was allowed to diffuse into a solution of H₂fan (32 mg, 0.15 mmol) in 4 mL of acetone with a 1:1 H₂O-acetone buffer solution under ambient conditions in air. Violet blocklike crystals suitable for X-ray diffraction appeared within 4 d. (Yield: 39.2 mg, 67.7%). IR (ATR): 2963 (w), 2933 (w), 2876 (w), 1645 (w), 1522 (s), 1495 (m), 1401 (s), 1376 (s), 1037 (w), 1005 (s). Anal. Calcd for $Zn_2C_{50}H_{72}N_2O_{18}F_6$:3H₂O: C, 50.38%; H, 6.60%; N, 2.27%. Found: C, 50.50%; H, 6.06%; N, 2.32%.

Synthesis of $Li_{0.27}\{(NBu_4)_2[Fe_2(fan)_3]\}$ (1·Reduced). A powdered sample of 1 (28 mg, 0.025 mmol) was suspended in a 0.1 M solution of lithium naphthalenide (0.25 mL, 0.025 mmol) and stirred for 3 h under an argon atmosphere. The suspension was filtered under argon and washed with anhydrous THF (3 × 1 mL) to yield a maroon solid (Yield: 20.8 mg). IR (ATR): 3238 (br), 2962 (w), 2875 (w), 1645 (w), 1532 (s), 1485 (m), 1346 (s), 1086 (w), 996 (w) cm⁻¹. Anal. Calcd for $Fe_2C_{50}H_{72}N_2O_{18}F_6Li_{0.27}$: C, 49.36%; H, 5.96%; N, 2.30%. Found: C, 50.40%; H, 6.17%; N, 2.25%.

Attempted Reduction of $(NBu_4)_2[Zn_2(fan)_3]$. A powdered sample of 2 (114 mg, 0.10 mmol) was suspended in a 0.1 M solution of lithium naphthalenide (1 mL, 0.1 mmol) and stirred for 3 h under an argon atmosphere. The suspension was filtered under argon and washed with anhydrous THF (3 × 1 mL) to yield a yellow solid. Powder diffraction indicated a loss of crystallinity. IR (ATR): 2962 (w), 2976 (w), 1645 (w), 1519 (m), 1489 (s), 1400 (m), 1373 (s), 1036 (w), 1003 (s) cm⁻¹.

Crystallography. Crystals of $(NBu_4)_2[Fe_2(fan)_3]$ and $(NBu_4)_2[Zn_2(fan)_3]$ were transferred directly from the mother liquor to a protective oil before being mounted on a goniometer in a cooled stream of nitrogen. Diffraction data for $(NBu_4)_2[Fe_2(fan)_3]$ were collected on an Oxford Diffraction SuperNova diffractometer, while the MX1 beamline at the Australian Synchrotron was used in the case of $(NBu_4)_2[Zn_2(fan)_3]$. The structures were solved using SHELXT¹⁸ and refined using a full-matrix least-squares procedure based upon $F^{2,19}$ Structure solution and refinement were performed within the WinGX system of programs.²⁰ Crystal information and details relating to the structural refinements are presented in Table 1. Further

Та	ble	1.	Crystal	Details	and	Refinement	for	1	and	2

	1	2
chemical formula	$C_{50}H_{72}F_{6}Fe_{2}N_{2}O_{12}$	$C_{50}H_{72}F_6N_2O_{12}Zn_2$
a, b (Å)	31.2842(7)	31.272(4)
c (Å)	19.6429(5)	19.711(2)
α, β, γ (deg)	90, 90, 120	90, 90, 120
V (Å ³)	16648.9(9)	16694(4)
Ζ	12	12
formula weight	1118.79	1137.83
space group	R3c	R3c
T (°C)	-143	-173
$D_{\rm calcd}~({\rm g~cm^{-3}})$	1.339	1.358
$\mu (\mathrm{cm}^{-1})$	4.867	0.940
$R(F_0) [I > 2\sigma(I)]$	0.0598	0.0777
$R_{\rm w}(F_0^2)$	0.1857	0.2180

crystallographic data are presented in Supporting Information, and CIF files have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1545608, $(NBu_4)_2[Fe_2(fan)_3]$ and 1545609, $(NBu_4)_2[Zn_2(fan)_3]$).

Mössbauer Spectroscopy. ⁵⁷Fe Mössbauer spectra were collected on a spectrometer from Science Engineering & Education (SEE) Co., MN, equipped with a closed cycle refrigerator system from Janis Research Co. and Sumitomo Heavy Industries Ltd. Data were collected in constant acceleration mode in transmission geometry. The zero velocity of the Mössbauer spectrum refers to the centroid of the room-temperature spectrum of a 25 μ m metallic iron foil. Analysis of the spectra was conducted using the WMOSS program (SEE Co., formerly WEB Research Co. Edina, MN).

Magnetism. Magnetic susceptibility measurements were made using a Quantum Design MPMS 7 Squid instrument in a directcurrent (dc) field of 1 T, with accurately weighed samples of ~25 mg placed in a calibrated gelatin capsule that was held in the center of a soda straw, the latter fixed to the sample rod. The instrument was calibrated with a palladium pellet (Quantum Design) or with a chemical calibrant such as $CuSO_4 \cdot SH_2O$ or $HgCo(NCS)_4$. The magnetization measurements were made on the same instrument with scan rate of 680 Oe/step employed between -5000 and 5000 Oe in Hyst mode, and scan rate of 3000 Oe/step between and -5000 and -5000 Oe and between 5000 and 50 000 Oe.

Conductivity. Conductivity measurements were performed on Quantum Design Physical Property Measurement System (PPMS) on pelletized samples using a linear four-point electrode. The temperature was controlled within the cryo-chamber of the PPMS with a ramp rate of -2 K min⁻¹. Unit resistivity was calculated according to the equation $\rho = RA/l$, where A = width × thickness, and l = 2 mm.

Electrochemistry and Spectroscopy. Cyclic voltammograms were collected on a BASi Epsilon electrochemical analyzer. All measurements were recorded in 0.1 M KCl/H₂O electrolyte using a glassy carbon electrode, platinum counter electrode, and a Ag/AgCl reference electrode in 3 M NaCl_(aq). All potentials are reported in volts versus Ag/AgCl. UV–vis–NIR (NIR = near-infrared) spectra were collected on an Agilent CARY5000 Spectrometer with a Harrick Omni-Diff probe. Spectra were collected between 5000 and 25 000 cm⁻¹ and are reported as the Kubelka–Munk transform, where $F(R) = (1 - R)^2/2R$. The spectra have been smoothed using the Savitzky–Golay function (30 points).

RESULTS AND DISCUSSION

Synthesis and Structure of $(NBu_4)_2[M_2(fan)_3]$ (M = Fe, Zn). The slow diffusion of H₂fan in acetone into an aqueous solution of FeCl₂·4H₂O and NBu₄Br yielded black polyfaceted crystals of the formula $(NBu_4)_2[Fe_2(fan)_3]$ (1) suitable for Xray diffraction. When $Zn(NO_3)_2$ ·6H₂O was used in place of FeCl₂·4H₂O an analogous compound with the formula $(NBu_4)_2[Zn_2(fan)_3]$ (2) was obtained. Investigations of the stability of these compounds using thermogravimetric analysis (TGA; Figure S1) indicate that chemical decomposition occurs at temperatures in excess of 250 °C.

A single-crystal X-ray diffraction investigation of 1 indicated the adoption of the trigonal space group R3c. There are two crystallographically distinct octahedral Fe centers, each of which is bound to three chelating and bridging fluoranilate ligands within a 3D coordination network (Figure 1a). One type of Fe center (Fe1) lies on a general position, while (Fe2) is located on a threefold axis. There are 3 times as many Fe1 centers as Fe2 centers. All Fe centers within a single network have the same absolute configuration, and this leads to the formation of a chiral network with the (10,3)-a topology (Figure 1b). In its geometrically most symmetrical form the (10,3)-a net consists of fourfold helices running in three mutually perpendicular directions; the smallest circuit involving the 3-connecting nodes is a non-planar decagon. Networks with the (10,3)-a topology are typically open-type structures with large intraframework voids and this network is no exception with the single network occupying only 35% of the crystal volume, based upon its van der Waals surface. The remaining space is occupied by a second symmetry-related network with the opposite configuration and countercations. The two interpenetrating networks form an enantiomeric pair, and thus the crystal exists as a racemate, schematically represented in Figure 1c. In addition to the metal centers possessing opposite configuration in the two networks, inspection of Figure 1c reveals that the fourfold helices in the two networks turn in opposing directions. Disordered tetrabutylammonium cations are located approximately midway between pairs of Fe centers belonging to the two networks. A space-filling representation of part of the two interpenetrating anionic networks is presented in Figure 1d, while Figure 1e shows a similar view with the tetrabutylammonium cations filling the spaces between the networks. A similar structure is obtained for 2 but with Zn in place of Fe. The structures of 1 and 2 provide an interesting contrast with the structures of $(NBu_4)_2[M_2(dhbq)_3]$ (M = Mn, Fe, Co, Ni, Zn, and Cd) reported in 2011, which are cubic in the case of M = Fe, Co, Ni, Zn, and Cd and tetragonal in the case of M = Mn. With the adoption of the cubic symmetry for $(NBu_4)_2[Fe_2(dhbq)_3]$ and



Figure 1. Structure of **1** showing (a) the coordination environments of the Fe centers, C black, O red, F green, Fe1 blue, Fe2 pink; Fe2 is located on a crystallographic threefold axis. (b) One of two (10,3)-*a* networks. (c) Schematic representation of the two independent (10,3)-*a* nets; spheres represent Fe centers (nodes), and connections represent bridging fan anions. (d) Space-filling representation of the two anionic networks (green and purple). (e) Space-filling representation of the two networks and the tetrabutylammonium countercations (red and blue).

 $(NBu_4)_2[Zn_2(dhbq)_3]$, all metal centers are symmetry related with each lying on a threefold axis.

As indicated in the Introduction, Long and co-workers spectroscopically showed that the Fe centers in

 $(NBu_4)_2[Fe_2(dhbq)_3]$ are Fe(III). Estimation of the oxidation state of the Fe center in $(NBu_4)_2[Fe_2(dhbq)_3]$ using bond valence sum (BVS) calculations^{21} (+2.98) are consistent with the spectroscopic assignment of the +3 oxidation state for the

Fe centers (see Supporting Information). Similarly, the Fe centers in $(NEt_4)_2[M_2(can)_3]^{15}$ and $(Me_2NH_2)_2[M_2(can)_3]^{12}$ are also close to +3 (+2.97 and +2.96, respectively). The crystal structure determination performed on $(NBu_4)_2[Fe_2(fan)_3]$, 1, reveal average Fe1-O and Fe2-O distances of 2.046 and 2.065 Å, respectively, which are significantly longer than the average Fe–O distances in $(NBu_4)_2$ [Fe₂(dhbq)₃] of 2.018 Å. BVS calculations based on the crystal structure of 1 lead to an estimation of a +2.76 oxidation state for Fe1 and a +2.61 oxidation state for Fe2. Given that there are 3 times as many Fe1 centers as Fe2 centers, the average oxidation state of the Fe in 1 is calculated to be +2.72. The average oxidation state of the anionic ligand must therefore lie somewhere between -2 and -3. With the BVS calculations for 1 suggesting that all Fe centers are intermediate between the +2 and +3 oxidation states, the formula of 1 may be formally represented as $(NBu_4)_4[Fe^{II}Fe^{III}_3(fan^{II-})_3(fan^{III-})_3]$. This formulation would suggest that the average oxidation state of the fluoranilate is -2.5 in contrast to $(NBu_4)_2[Fe_2(dhbq)_3]$, where the average oxidation state of the dhbq is -2.67. In the $(NBu_4)_4[Fe^{II}Fe^{III}_3 (fan^{II-})_3(fan^{III-})_3$ formulation, the average oxidation state of the Fe would be +2.75. While the proposed formulation of $(NBu_4)_4$ [Fe^{II}Fe^{III}₃(fan^{II-})₃(fan^{III-})₃] is only tentative, the structural results suggest an average oxidation state for the Fe of somewhere between +2.5 and +3.0.

While the strong structural similarities that exist between 1 and 2 are clearly apparent, there are subtle but significant differences between the two structures that largely arise from the fact that the zinc center is limited to the +2 oxidation state. To achieve charge balance in $(NBu_4)_2[Zn_2(fan)_3]$ the fluoranilate dianion must be in the -2 oxidation state. Ligand bond distances for the dianion are consistent with the adoption of the quinone form of the ligand. In particular, the C-C separations within the five-membered chelate rings (1.525(10), 1.533(10) Å) are consistent with a formal single bond. In the case of 1 the corresponding bond distances are 1.494(10) and 1.486(10) Å, which indicate some multiple bond character, consistent with partial reduction of the dianion.

Mössbauer Spectroscopy. The results from the BVS calculations coupled with investigations of the related dhbq network, (NBu₄)₂[Fe₂(dhbq)₃], prompted further examination of the oxidation state of the Fe centers in 1 using variable-temperature ⁵⁷Fe Mössbauer spectroscopy. The spectra are given in Figure 2, and the parameters are in Table 2. At 293 K the spectrum shows the presence of at least two components, namely, a broad quadrupole doublet with parameters ($\delta = 0.56$, $\Delta E_Q = 1.22$ mm/s) that is consistent with high spin iron(III), and a broad singlet ($\delta = 0.55$ mm/s) that indicates intermediate relaxation.

The absence of a subspectrum describing iron(II) suggests that the system is valence-delocalized and that the high-spin iron(III) quadrupole doublet actually describes a ca. +2.7 oxidation state as supported by the other data. The large half height width of the quadrupole doublet could perhaps be explained by the presence of multiple sites, which cannot be separated, but as the temperature is lowered, both the intermediate relaxing singlet and the quadrupole doublet broadens and turns into the very broad magnetic spectrum collected when the sample is cooled to 5.5 K. It thus seems more likely that the broadness is due to the intermediate relaxation regime that the sample exhibits.

The magnetic spectrum measured at 5.5 K can be used as a reference and subtracted from all other spectra to help



Figure 2. Variable-temperature ⁵⁷Fe Mössbauer spectra of 1 measured in the presence of a weak magnetic field of 47 mT applied parallel to the γ -rays. The spectra can be deconvoluted into a mixture of slow relaxing (black dotted, spectrum measured at 5.5 K), intermediate relaxing (red), and fast relaxing (blue) high-spin iron(III). The total fit is given by the solid black lines through the hatch marks.

Table 2. Temperature-Dependent 57 Fe Mössbauer Parameters Obtained for 1^a

T (K)	$\delta ~({ m mm/s})$	$\Delta E_{\rm Q} ({\rm mm/s})$	$\Gamma_{L(R)} \ (mm/s)$
293	0.56 ± 0.02	1.22 ± 0.04	0.59(0.59)
	0.55 ± 0.05^{b}	0	0.70
200	0.59 ± 0.01	1.24 ± 0.02	0.39(0.43)
	0.55 ± 0.03^{b}	0	0.60
100	0.59 ± 0.01	1.27 ± 0.03	0.38(0.45)
50	0.59 ± 0.01	1.28 ± 0.02	0.42(0.50)

^{*a*}All spectra contain a proportion of a broad magnetic spectrum caused by ferromagnetic coupling that is fully observed at 5.5 K. ^{*b*}This appears to be caused by intermediate relaxation.

determine relative areas and aid fitting of the other two components. With this method it can be seen that the quadrupole doublet decreases in intensity, until at 5.5 K the system is fully ferromagnetic. This magnetic transition occurs over a wide temperature range (Figure 3) and is supported by the magnetic studies (vide infra). The broad magnetic spectrum collected at ~5 K is indicative of ferromagnetic coupling with an internal field $B_0 \approx 50$ T.

The parameters of the quadrupole doublet vary slightly with temperature with a slight increase in quadrupole splitting, and this can be ascribed to the second-order Doppler effect.²² Interestingly, the parameters obtained at 100 K are identical to those also measured at 100 K for the related unfluorinated compound described previously¹¹ and similar to those reported



Figure 3. Proportion of each species determined by ⁵⁷Fe Mössbauer is plotted against temperature. The slow-relaxing iron(III) (\bigcirc) is caused by ferromagnetic coupling between iron centers. The fast-relaxing iron(III) (\Box) is a quadrupole doublet consistent with high-spin iron(III), and intermediate relaxation is observed as a broad singlet (\triangle). Both of these species converts into the slow-relaxing subspectrum. Spectra are presented in Figure 2, and parameters are given in Table 2.

at 80 K for $(Me_2NH_2)_2[Fe_2(can)_3]\cdot 2H_2O\cdot 6DMF$, the latter showing a lower value of ΔE_Q (1.059(2)),¹² which increased a little upon desolvation.

Magnetism. It is well-recognized that the tetraoxolene class of ligands are able to mediate magnetic interaction between metals. Discrete binuclear complexes in which metal centers are linked by anionic forms of H2dhbq and H2can have demonstrated the ability to exist in a mixed-valence state, whereby valence-tautomerism occurs via redox modulation of the ligand via their radical trianion state.^{23,24} 2D coordination polymers of the form $[M_2(C_6O_4X_2)_3]^{n+}$ have been shown to exhibit long-ranged ferri-^{25,26} or ferromagnetic coupling mediated by the di-anionic form of $(C_6O_4X_2)^{2-}$, while an example of a 3D framework of diamond-topology with the formula $Na_5[Ho^{III}(THB^{IV-})_2] \cdot 7H_2O$ (H₄THB = 1,2,4,5tetrahydroxybenzene), which remarkably incorporates the fully reduced form of dhbq de novo, was shown to be ferromagnetic.²⁷ In view of the crystal structure of 1, it was anticipated that a strong electronic communication between adjacent iron centers via fan²⁻/fan³⁻ would give rise to longrange and ferromagnetic magnetic ordering.

Temperature-dependent magnetic studies of 1 under applied fields of 0.0087, 0.1, and 1 T were conducted, and the graph of $\chi_{\rm M}T$ versus T is presented below (Figure 4). The data are independent of the field value between 70 and 300 K but



Figure 4. Plot of $\chi_M T$ vs temperature and a magnetization vs field plot (inset) of 1 at 2 and 10 K.

dependent on field below 70 K, with a broad maximum of 33 $cm^3 mol^{-1}$ K, at 50 K, found in the 1 T field, becoming sharper and higher in value, 111 cm³ mol⁻¹ K, at 5 K, in the 0.0087 T field. Such behavior is indicative of a combination of Zeeman level thermal depopulation effects combined with either magnetic coupling or magnetic order. For compound 1, a $\chi_{\rm M}T$ of 8.22 cm³ mol⁻¹ K, per Fe₂, at 300 K was observed, which is a little lower than that predicted for the uncoupled "two Fe site" formulation $(NBu_4)_4[Fe^{II}Fe^{III}_3(fan^{II-})_3(fan^{III-})_3]$ (vide supra) containing 1/2[HS Fe^{II}, HS Fe^{III} × 3 and S = 1/2 $(fan^{III-}) \times 3$] of 8.62 cm³ mol⁻¹ K, per Fe₂. The 300 K $\chi_M T$ value observed for (NBu₄)₂[Fe₂(dhbq)₃] was 11.11 cm³ mol⁻¹ K, significantly higher than in 1.¹¹ It showed a similar plot to that of 1, in a 0.1 T field, with a sharp maximum of 150 cm³ mol^{-1} K at ~10 K, thus behaving, overall in a similar fashion to 1. However, it was formulated as $(NBu_4)_2[Fe^{III}_2(dhbq^{II-}) (dhbq^{III-})_2]$, which would give a predicted $\chi_M T$ of 9.5 cm³ mol⁻¹ K, per Fe₂, at 300 K assuming zero/very weak coupling at this temperature. Likewise, an even higher $\chi_{\rm M}T$ of 16.6 cm³ mol^{-1} K, per Fe₂, was reported, at 300 K, for $(Me_2NH_2)_2$ $[Fe^{III}_2(can^{II-})(can^{III-})_2]\cdot 2H_2O\cdot 6DMF$ and ascribed to longrange strong magnetic coupling. Interestingly, it decreased to 9.37 cm³ mol⁻¹ K, at 300 K, for the desolvated species.¹²

When the temperature was decreased, the gradual increase in $\chi_M T$ for **1** is usually indicative of ferromagnetic coupling, with the rapid increase below 70 K indicative of short- or long-range ordering of Fe and radical spins. The $\chi_M T$ maximum value in the 1 T field of 33 cm³ mol⁻¹ K, per Fe₂, is as predicted for ferromagnetic coupling yielding a ground-state spin S = [5/2 + 5/2 + 5/2 + 4/2 + 1/2 + 1/2 + 1/2] = 22/2, per Fe₄). The much higher $\chi_M T$ maxima in lower fields lend support for magnetic ordering occurring. The decrease in $\chi_M T$ below the maximum can originate from Zeeman level depopulation effects or from anti-ferromagnetic coupling occurring at very low temperatures.

Magnetization isotherms were measured on 1 to help delineate the type of magnetic order (Figure 4; inset). They show close to saturation behavior at 2 K, above $H \approx 4$ T, with $M \approx 7.3 \ N\beta$. This is well below the ~11 $N\beta$ expected for S =11/2, per Fe₂, using the (NBu₄)₄[Fe^{II}Fe^{III}₃(fan^{II-})₃(fan^{III-})₃] formulation (see above) and a little lower than 8 $N\beta$ expected for a S = 4 ground state (S = 5/2 + 5/2 - 1/2 - 1/2 = 8/2) if antiferrimagnetic coupling was occurring in a (NBu₄)₂[Fe^{III}₂(dhbq^{II-})(dhbq^{III-})₂] type formulation.¹¹ Interestingly, the dhbq compound also showed M_{sat} of 7.2 $N\beta$. The solvated chloranilate analog reached M = 8.2 $N\beta$ in H = 7 T at 1.8 K,¹² close to the S = 4 ground state value, and showed hysteresis with a much bigger coercive field of 2630 Oe, at 1.8 K. The coercive field increased to 4650 Oe for the desolvated chloranilate.

A common way to check for long-range (3D) magnetic order is to measure the field-cooled (FCM) and zero-field cooled magnetization (ZFCM) in small dc fields, at low temperatures, with bifurcation in FCM and ZFCM indicative of long-range order. These plots (Figure S5) overlay for 1, thus indicating that only short-range order is occurring down to 2 K. In contrast, $(Me_2NH_2)_2$ [Fe^{III}₂(can^{II-})(can^{III-})₂]·2H₂O·6DMF bifurcation of FCM and ZFCM below 80 K is indicative of spontaneous magnetization due to dominant intralayer antiferromagnetic interactions.¹² Recently, Harris et al. reported the o n e - e l e c t r o n r e d u c e d c o m p l e x $(Cp_2Co)_{1.43}(Me_2NH_2)_{1.57}$ [Fe₂(can)₃]·4.9DMF, which contains the framework composition [Fe^{III}₂(can^{III-})₃]³⁻, and showing a $\chi_{\rm M}T$ value of 26.5 cm³ mol⁻¹ K at 300 K much higher than the 9.875 cm³ mol⁻¹ K uncoupled value. This was due to strong magnetic ordering evidenced by bifurcation of FCM and ZFCM at 115 K and large coercive fields (4520 Oe at 1.8 K) in the magnetization isotherms, the coupling being stronger than that in (Me₂NH₂)₂[Fe^{III}₂(can^{III}-)(can^{III-})₂]·2H₂O·6DMF.¹³ The short-range order in **1**, also noted in

The short-range order in 1, also noted in $(NBu_4)_2[Fe_2(dhbq)_3]^{,11}$ is possibly due to competing ferromagnetic and anti-ferromagnetic interactions that prevents 3D order. It is tempting to ascribe such behavior, in part, to through-space interactions between the interpenetrated sublattices in 1, but we have no direct evidence for this. The magnetic interactions occur via the radical-bridged Fe^{II/III} centers in the individual (10,3)-*a* networks.

Electrochemical and Spectroscopic Properties. Solidstate dc cyclic voltammetry was performed on 1 in 0.1 M KCl/ H_2O electrolyte at multiple scan rate (Figure S7); a representation of the 200 mV s⁻¹ scan is presented in Figure 5. In the cyclic voltammograms (CVs) of 1, two broad *quasi*-



Figure 5. Solid-state CV of 1 at 200 mV in 0.1 M KCl/H₂O electrolyte.

reversible processes are evident from the cathodic sweep at -0.25 and -0.80 V versus Ag/AgCl. While the process occurring at -0.25 V is apparent at fast scan rates (1000 mV s⁻¹), it is barely apparent at slower scan rates, for example, 200 mV s⁻¹. The second reduction process (-0.80 V) is clearly present at all scan rates. The return anodic sweep shows two distinct oxidation processes at -0.65 and 0.25 V.

The CVs are somewhat more complicated than that obtained for the compound $(PMePh_3)_2[Cd_2(dhbq)_3]$ reported in 2012 in which octahedral Cd(II) centers are linked by dhbq²⁻ anions within a 2D hexagonal network.¹⁰ In the case of the Cd network the CV indicated a reduction at -0.68 V and return oxidation at -0.51 V, which was attributed to the reversible reduction of the dhbq²⁻ ions in the network to their tetraanionic form. The solution-state CV for fluoranilic acid shows similar redox behavior with reduction at -0.19 V and a return oxidation at 0.01 V (Figure S6). In the case of 1 the accessibility of two stable oxidation states for Fe and redox behavior of the fluoranilate makes assignment of the electrochemical processes more challenging, not just because an additional component of the network is redox-active (Fe) but because the iron centers and fluoranilate are not expected to act in isolation from each other. The interdependence of the oxidation states is neatly illustrated by some elegant work undertaken by Dei, Gatteschi, and co-workers in 1991.²⁸ In a discrete binuclear complex in which a pair of Fe(II) centers are linked by a dhbq dianion, a *one*-electron oxidation of the complex resulted in oxidation of *both* Fe(II) centers to Fe(III) accompanied by a reduction of the bridging dianion to the radical trianion. Thus, while it may be tempting to ascribe the reduction and oxidation processes at -0.80 and -0.65 V, respectively, to ligand-based processes, such changes in oxidation state may also be accompanied by changes in the oxidation state of the Fe centers. The solid-state CV for **2** (Figure S8) fails to provide a useful comparison, as the only clearly defined process is an irreversible oxidation process at -0.65 V. The electrochemical results are consistent with decomposition and dissolution of **2**.

The broadness, together with the shifting of processes at higher scan rates, suggests the observed processes for 1 and 2 are surface-confined as a result of the lack of diffusion of counterions necessary for charge balance of the framework as observed in similar systems.¹⁰ The results presented here illustrate the stability of 1 to electrochemical treatment, whereby the framework was able to undergo multiple redox cycles while retaining reversibility in the solid state. Thus, 1 was further studied via solid-state spectro-electrochemistry to probe the redox modulation in situ.

Solid-state SEC²⁹ studies were conducted on 1 in 0.1 M KCl/H₂O electrolyte to investigate the optical properties. The UV–vis–NIR spectrum of the as-synthesized species shows three distinct features as shown in Figure 6; the broad bands



Figure 6. Solid-state SEC of 1 in 0.1 M KCl/H₂O electrolyte and pictures (inset) of 1 undergoing progressive stages of reduction at the indium tin oxide interface (right). Arrows indicate the direction of the spectral progression. The break in the spectrum denotes the region of the detector changeover, which was removed for clarity.

that appear at ca. 17 500 and 21 000 cm⁻¹ are tentatively assigned to $\pi - \pi^*$ and metal-to-ligand charge transfer (MLCT) transitions, respectively, while the intense band observed in the near-IR region (ca. 7000 cm⁻¹) is tentatively assigned to a ligand-based IVCT band. Application of a reductive potential of -0.9 V leads to the decrease in the bands and overall absorbance of the sample. The decrease of the IVCT band may be rationalized as the result of reduction of the fluoranilate ligand from fan^{2–} to fan^{4–} via the radical trianion form (fan^{3–}). A notable color change was observed upon reduction of the material from dark brown/black to a light yellow/maroon (Figure 6, inset) providing evidence supporting the reduction of **1**. Attempts to reoxidize the sample through application of an oxidative potential led to an incomplete regeneration of the original spectrum (see Supporting Information, Figure S10).

The observation of the IVCT band in 1 is consistent with a rare mixed-valence state,³⁰ whereby the Fe centers and fan ligands possess noninteger redox states. Postsynthetic reduction studies were undertaken to further examine the redox activity of 1.

Chemical Reduction. To verify the SEC experiments, chemical reduction of 1 and 2 was performed ex situ through the addition of excess lithium napthalenide (1 equiv) under an inert atmosphere. ICP-OES studies revealed that 1 could be reduced to $\text{Li}_{0.27}\{(\text{NBu}_4)_2[\text{Fe}_2(\text{fan})_3]\}$ (1•Reduced). The powder X-ray diffraction (PXRD) pattern (Figure S2) of 1• Reduced indicates that the structure remains unchanged with only minor deterioration in the crystallinity of the sample apparent upon reduction. The attempted reduction of 2 with lithium naphthalenide leads to a significant loss in the crystallinity of the sample as evident from the PXRD (Figure S3) and a color change of 2 from violet to light yellow. This is consistent with the formation of the tetraanion form of fluoranilate and decomposition of the framework to form an unidentified residual product.

The solid-state UV-vis-NIR spectrum of 1.Reduced (Figure 7a) revealed spectral changes akin to those found in the SEC measurements, which showed the IVCT band in the NIR region diminishing and the broad MLCT bands decreasing in intensity upon electrochemical reduction. Interestingly, the vis-NIR spectrum of 2 (Figure 7a) displays a complete absence of the low-energy IVCT band and MLCT band present in 1, further supporting the evidence that partial charge transfer between ligands is mediated by iron, which provides a more optimal frontier-orbital overlap than zinc. In addition, solidstate EPR studies (Figure 7b) on 1 revealed the presence of a radical signal (g = 2.00735) attributed to the radical trianion, fan³⁻. Upon chemical reduction to 1.Reduced, a radical signal persists (g = 2.00043). We propose that the intercalation of Li⁺ ions, for charge balance, is accompanied by the generation of a greater proportion of fan³⁻. In contrast, the EPR spectrum of 2 indicates the absence of radical species.

The differences between 1 and 1•Reduced were investigated using Raman spectroscopy (Figure S11). A spectrum of each compound was obtained using an 830 nm laser. Very little difference exists between the spectra for the two compounds except for a peak at 1650 cm⁻¹ in the case of 1•Reduced. The spectrum for fluoranilic acid (Figure S12) is significantly different than 1 and 1•Reduced, although it does show a strong peak at 1650 cm⁻¹.

Electrical Conductivity. The elucidation of the electrochemical and optical properties of 1 encouraged us to explore the electronic properties of the framework. Investigation of the temperature-dependent conductivity via the four-point contact method on a pelletized sample of 1 (Figure 8) revealed semiconducting behavior at room temperature (ca. 5.5×10^{-3} S/cm). An Arrhenius fit of the conductivity data (Figure S13) showed that 1 possesses an activation energy of just 124 meV. I-V curve measurements were conducted via four-point contact probe on a pressed pellet of 1 (Figure S15). The room-temperature conductivity was found to be 1.77×10^{-3} S/ cm and Ohmic in the scan range of ± 10 mV. The bulk





Figure 7. (a) UV-vis-NIR spectrum of 1 (black), 1•Reduced (red), and 2 (blue). (b) EPR spectrum of 1 (black) and 1•Reduced at room temperature.



Figure 8. Variable-temperature conductivity of **1** between 165 and 300 K.

conductivity of 1, however, deviates from the compound reported by Long et al.¹¹ This discrepancy may indicate a larger number of defects or grain boundaries present in our sample.

We may also postulate the lower conductivity of 1 to arise from the lower crystal symmetry setting (rhombohedral) as compared to the cubic structure of $(NBu_4)_2[Fe_2(dhbq)_3]$. From an anisotropy perspective our (10,3)-a framework may introduce a directional factor, commonly encountered in "organic metal" complexes that may explain the observed electrical conductivity. Additionally, the lower conductivity observed for 1 in contrast to $(NBu_4)_2[Fe_2(dhbq)_3]$ could be the result of air oxidation of fan³⁻ in the as-synthesized framework of 1 to fan²⁻. Finally, variation in the devices used for conductance measurements as well as the environment can significantly impact upon conductance measurements. As Dincă and co-workers have clearly stated with respect to conductivities of MOF-type materials, "accurate measurements of intrinsic electrical conductivity are challenging and fraught with potential sources of errors."³¹ They further indicate that caution needs to be exercised when comparing measured conductivities that vary by up to 2 orders of magnitude.

In a discussion of conductivity by Long and co-workers¹¹ it was suggested that the conductivity of $(NBu_4)_2[Fe_2(dhbq)_3]$ is linked to electron hopping between the dhbq²⁻/dhbq³⁻ manifold. The excess of electron-rich dhbq3- ligands over the electron-deficient dhbq²⁻ ligands is considered to be less than ideal as far conductivity is concerned. This is supported by the observation that a chemically reduced form, $Na_{0.9}(NBu_4)_{1.8}[Fe_2(dhbq)_3]$, which possesses a higher proportion of the trianion radicals, has a significantly lower conductivity than (NBu₄)₂[Fe₂(dhbq)₃]. Long and co-workers further proposed that partial oxidation of $(NBu_4)_2[Fe_2(dhbq)_3]$ to generate a material in which the relative proportions of dhbq³⁻ and dhbq²⁻ are similar may yield a compound with superior conductivity. On this basis, compound 1, with the tentatively proposed formulation of $(NBu_4)_4$ [Fe^{II}Fe^{III}₃(fan^{II-})₃(fan^{II-})₃], involving equal numbers of fan²⁻ and fan³⁻ ligands, might have been expected to be a significantly better conductor than our results indicated.

CONCLUSIONS

Although 1 and 2 share a similar composition and structure in which octahedral metal centers are linked by fluoranilate ligands, there is a stark contrast in the physical behavior of the two compounds. While the Zn(II) centers in $(NBu_4)_2[Zn_2(fan)_3]$ are clearly linked by fluoranilate dianions, Mössbauer spectroscopy indicates that Fe centers are in an oxidation state close to +3 in 1, and as a result the average oxidation state of the fluoranilate lies between -2.5 and -3.0. While Fe-O bond distances, determined by X-ray crystallography, also support the assignment of an oxidation state for the Fe centers that is clearly greater than +2, they are slightly longer than the corresponding bond lengths in $(NBu_4)_2[Fe_2(dhbq)_3]$ with BVS calculations suggesting an average oxidation state for the Fe centers of ca. +2.75. On this basis the formula of the compound could be represented a s $(NBu_4)_4[Fe^{II}Fe^{III}_3(fan^{II-})_3(fan^{III-})_3]$. This formulation contrasts with that proposed for the dhbq analogue, which may be represented as $(NBu_4)_2[Fe^{III}_2(dhbq^{II-})(dhbq^{III-})_2]$ according to both Mössbauer spectroscopy¹¹ and BVS calculations. In making these comparisons it is important to recognize that BVS calculations provide only a crude estimation of oxidation states, and as a consequence, the assignment of the oxidation states in $(NBu_4)_2[Fe_2(fan)_3]$ should be viewed with caution.

The magnetic behaviors of 1 and $(NBu_4)_2[Fe^{III}_2(dhbq)_3]^{,11}$ $(Me_2NH_2)_2[Fe^{III}_2(can)_3] \cdot 2H_2O \cdot 6DMF^{,12}_{,12}$ and

 $(Me_2NH_2)_2[Fe_2^{III}(can)_3]$ show many similarities but also significant differences. The similarities in 1 and $(NBu_4)_2$ [Fe^{III}₂(dhbq)₃], that is, short-range magnetic order, derive from their similar crystal structures and metal/ligand electronic structures, although the latter also has differences because of the different Fe oxidation states and bridging ligand II-/III- states proposed for 1 and for the dhbg analogue. While $(Me_2NH_2)_2[Fe^{III}_2(can)_3] \cdot 2H_2O \cdot 6DMF$ and (NBu₄)₂[Fe^{III}₂(dhbq)₃] have similar Fe and ligand oxidation states, the long-range order in $(Me_2NH_2)_2$ [Fe^{III}₂(can)₃]·2H₂O· 6DMF, a 2D magnet with $T_c = 80$ K, is much stronger than it is in $(NBu_4)_2[Fe^{III}_2(dhbq)_3]$. It is even stronger in the compound $(Cp_2Co)_{1,43}(Me_2NH_2)_{1,57}[Fe_2(can)_3] \cdot 4.9DMF$ that contains three can^{3–} radicals; a possible bulk 2D ferrimagnet with T_c = 105 K. Nevertheless, patterns can be discerned in the magnetic behaviors of these above-mentioned $[Fe_2L_3]^{n-1}$ framework family members that relate to the $Fe^{II/III}$ and ligand L^{II-/III-} oxidation states and relative ratios thereof, as well as to subtle structural differences. Furthermore, changing the substituents on the anilate ligand has a significant effect upon iron site symmetry and the magnetic features of members of this structurally similar family. In regard to the magnetic features, we note that Atzori et al.³² reported the influence of changing the substituent on the bridging, diamagnetic anilate ligand in isostructural 2D molecular ferrimagnets of type $\widetilde{A[Mn^{II}Cr^{III}(X_2An)_3]}$ ·G (A = [(H₃O)(phz)₃]+ (phz = phenazine) or NBu₄⁺; $X_2An^{2-} = C_6O_4X_2^{2-} = 2,5$ -dihydroxy-1,4-benzoquinone derivative dianion; X = Cl, Br, I, H; G = water or acetone. The ordering temperature changed from 5.5 to 6.3, 8.2, and 11.0 K (for X = Cl, Br, I, and H, respectively). A plot of T_c versus the electronegativity of X showed a clear linear correlation that was explained by the electron-withdrawing effect of X: as the electronegativity of X increases, the electron density in the anilato ring decreases, resulting in a weaker coupling and, therefore, in a lower T_{c} , thus allowing the tuning of the magnetic order. Further discussion of the effect of substituents on anilate ligands is presented in a recent review by Mercuri et al.³³ In the present $[Fe_2(X_2An)_3]^{2-}$ family, involving X_2An^{2-} and X_2An^{3-} bridging forms, where X = F (fan; present work), Cl (can), and H (dhbq) the substituents range from the most electronegative, F, to the least, H. Unfortunately, because of the many contributing factors such as the effects of cation upon network structures, and the mixed-valent nature of the Fe and bridging ligand centers in family members, it is not possible to detect clear correlations with variation in X groups. For example, $(NBu_4)_4$ [Fe^{II}Fe^{III}₃(fan^{II-})₃(fan^{III-})], **1**, and $(NBu_4)_2$ [Fe^{III}₂(dhbq^{II-})(dhbq^{III-})₂] show similar magnetism and degree of magnetic coupling.

Also with respect to the magnetic measurements, note that the coexistence of semiconductivity, with attendant bandstructure, and molecular magnetism in the fan and dhbq materials means that itinerant electrons do not dominate the magnetic features.

Electrochemical and spectro-electrochemical investigations in addition to chemical reduction reveal that the fluoranilate ligands in both 1 and 2 are susceptible to reduction. In the case of 1 the reduction is accompanied by a decrease in the intensity of the absorption bands in the UV-vis-NIR spectrum, which is consistent with the partial conversion of the fluoranilate ion to its aromatic tetraanionic form, which is colorless.

Conductivity measurements have unambiguously indicated that **1** is a semiconductor; however, the conductivity at room temperature $(5.5 \times 10^{-3} \text{ S/cm})$ is significantly less than that

found for $(NBu_4)_2[Fe^{III}_2(dhbq)_3]$. Nevertheless, in both compounds it would seem that the mixed valency of the ligands is an important feature, and this provides a basis for designing new coordination polymers that are electrical conductors.

This current work provides a strong indication that coordination networks derived from dhbq and related ligands have outstanding potential as materials possessing unusual and possibly useful magnetic and electronic properties. The ability of dhbq-type ligands to exist in multiple oxidation states within a network offers the prospect of mixed valency, which clearly impacts upon the electrical conductivity of the solid material. As this current work has demonstrated, the incorporation of metal ions that have multiple stable oxidation states will also have a significant effect on the physical properties of the network material. The opportunity to include a wide variety of organic countercations provides a means for controlling network topology, while the use of a counterion that is redox-active may allow the cation to participate in electron transfer processes with the anionic network. Porosity is another feature that may be controlled by choice of cation, with open channels allowing the introduction or removal of ions upon changes in the oxidation state of the anionic network. The presence of pores in the crystal structure provides an opportunity for introducing electron donors or acceptors as guests that may modulate the electronic and magnetic behavior of the network.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01038.

Details of experimentation, bond-valence-sum calculations, tabulated data including R_0 and B values, estimated Fe oxidation states, bond distances, crystal data and structure refinement, thermogravimetric and differential scanning calorimetric analyses, PXRDs, ⁵⁷Fe Mössbauer spectrum, plotted magnetic data, cyclic and square-wave voltammograms, Raman spectra, Tauc plots, Arrhenius plots, I-V plots, additional references (PDF)

Accession Codes

CCDC 1545608–1545609 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: bfa@unimelb.edu.au. Phone: +61 3 8344 0341. Fax: +61 3 9347 5180. (B.F.A.)

*E-mail: deanna.dalessandro@sydney.edu.au. Phone +61 2 9351 3777. Fax: +61 3 9351 3329. (D.M.D.)

*E-mail: r.robson@unimelb.edu.au. Phone: +61 3 8344 6469. Fax: +61 3 9347 5180. (R.R.)

ORCID 💿

Brendan F. Abrahams: 0000-0003-2957-860X

Present Address

△School of Chemistry, Bio21 Molecular Science and Biotechnology Institute, 30 Flemington Road, The University of Melbourne, Parkville Victoria 3052, Australia.

Notes

The authors declare no competing financial interest.

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