

A Bimodal Oxobenzene-bridged Bisdithiazolyl Radical Conductor

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Supporting Information

ABSTRACT: The preparation and structural characterization of the methyl-substituted oxobenzene-bridged bisdithiazolyl radical **3b** is described. Crystals of **3b** belong to the monoclinic space group C2/c and contain two distinct radical environments, **A** and **B**. There are eight **A** radicals in the unit cell, which occupy general positions and form alternating twisted π -stacks running parallel to the *c*-axis. The four **B** radicals also adopt an alternating π -stack pattern, but each molecule lies on a crystallographic 2-fold rotation axis, and the overlay of neighboring radicals is centrosymmetric. Stacks of **A** radicals are linked by close intermolecular S····O' and S····N' contacts into ribbon-like arrays that



weave along the *y*-direction, and the **B** radical stacks are located in columnar cavities generated by the out-of-register alignment of the ribbons of **A** radicals. Variable temperature magnetic susceptibility measurements indicate a strongly antiferromagnetically coupled system, a result in accord with DFT estimated exchange energies for intrastack radical–radical interactions. Four-probe conductivity measurements indicate a conductivity $\sigma(300 \text{ K}) = 9.0 \times 10^{-4} \text{ S cm}^{-1}$, with a thermal activation energy $E_{act} = 0.13 \text{ eV}$.

INTRODUCTION

The idea that the unpaired electron in a neutral organic radical might serve as a carrier of charge, thereby allowing the development of single component molecular metals with a half-filled (f = 1/2) energy band, was first proposed by Haddon in 1975.¹ In practice, however, the realization of conductivity in carbon-based radicals has not been easy, although considerable progress has been made in recent years by using phenalenyls and spirophenalenyls.² Other potential building blocks include highly stable, light heteroatom (N, O) radicals, such as aminyls, nitroxyls, and verdazyls,³ but in these systems spin density is too localized, and intermolecular hopping of the unpaired electrons is suppressed by the large onsite Coulomb repulsion associated with the f = 1/2 band structure.⁴

Heavy atom radicals, notably thiazyls and selenazyls, have also been pursued as building blocks for conductive materials,⁵ in the belief that the expected strong overlap between orbitals on neighboring sulfur (or selenium) atoms will increase solid state bandwidth W and hence facilitate charge migration. However, when coupled with the relatively confined spin distribution inherent in early heterocyclic thiazyls, this increased orbital overlap led to a pronounced tendency for radical association. More importantly spin localization caused a high onsite Coulomb repulsion energy $U_{,}^{6}$ so that even when dimerization could be avoided, intermolecular overlap and the resulting bandwidth were still insufficient to overcome charge repulsion, and conductivity was low.⁷ While dramatic improvements in conductivity could be induced by p-type doping,⁸ the restricted spin distribution in the neutral (f = 1/2) materials remained a serious impediment to their use in the design of purely neutral, single component systems.

The development of *N-alkylated* pyridine-bridged bisdithiazolyl radicals **1** (Chart 1) represented a major step forward, as



resonance stabilization between the two dithiazolyl "wings" effectively doubled spin delocalization.⁹ Consistently, the gas phase disproportionation energies $\Delta H_{\rm disp}$ and solution-based electrochemical cell potentials $E_{\rm cell}^{10}$ of these radicals, which provide indirect measures of U, were significantly reduced relative to those of earlier monocyclic derivatives. However, most examples of 1 crystallized as slipped π -stack arrays locked into herringbone packing patterns (Figure 1a), a motif which compromised bandwidth W and hence charge transport, although replacement of sulfur by its more spatially extensive congener selenium afforded significant improvements in both conductivity¹¹ and magnetic properties.¹² Isoelectronic replacement of the basal CR₂ unit by nitrogen, as in the *N*-alkylated

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Figure 1. Packing motifs found in 1, 2, and 3: (a) herringbone π -stacks, (b) alternating head-over-tail π -stacks, and (c) slipped ribbon π -stacks.

pyrazine-bridged radicals **2**, afforded new solid state structure types. Thus, while removal of the steric protection afforded by the basal ligand rendered the ethyl derivative **2b** susceptible to dimerization,¹³ the corresponding methyl compound **2a** displayed an alternating ABABAB π -stack structure (Figure 1b),¹⁴ the bandwidth and conductivity of which were dramatically improved relative to those seen in the herringbone structures adopted by **1**. However, at low temperatures (<120 K) the evenly spaced π -stacks of **2a** collapsed into dimers.

To break the herringbone mold found in 1, while at the same time avoiding the spin-quenching dimerization found for 2, we are currently exploring the structural and transport properties of radicals based on the resonance stabilized, oxobenzenebridged bisdithiazolyl framework 3, in which the NR₁ moiety of 1 is replaced by a carbonyl group. While the molecular electronic structure of these new radicals is similar to that of 1, the polarity of the carbonyl CO bond leads to the development of strong intermolecular S…O' interactions¹⁵ in the solid state. These supramolecular synthons¹⁶ are capable of generating rigid, ribbon-like arrays which pack as slipped π -stacks (Figure 1c) and afford improved charge transport.

Here we expand on our recent work on the chloro- and phenyl-substituted derivatives $3a^{17}$ and 3c,¹⁸ and describe the preparation and structural characterization of the methyl-substituted compound 3b (R = Me).¹⁹ From a structural perspective this latter material has proved particularly interesting, as it contains two crystallographically distinct radical environments, one packed within the superstructure created by the other. Variable temperature magnetic susceptibility and conductivity measurements on 3b are reported, and the results interpreted in the light of Density Functional Theory (DFT) and Extended Hückel Theory (EHT) band electronic structure calculations.

RESULTS

Synthesis and Electrochemistry. The preparative sequence to the oxobenzene-bridged bis-1,2,3-dithiazolyl 3b (Scheme 1) starts from 2,6-dinitro-p-cresol 4 which, upon reduction with Sn/HCl yields the bishydrochloride of 2,6diamino-4-methylphenol 5. This latter compound undergoes a double Herz cyclization with sulfur monochloride at reflux in acetonitrile to afford the chloride salt [3b][Cl] as an insoluble purple-brown powder. This material can be converted into the more soluble triflate (OTf⁻) salt by metathesis with silver triflate. The choice of reducing agent for the conversion of the salt [3b][OTf] to the neutral radical 3b was made on the basis of cyclic voltammetric (CV) measurements on solutions of [3b][OTf] in MeCN, with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte and Pt wire electrodes. As may be seen from the compilation of half-wave potentials listed in Table 1, there are some differences in the potentials for the reversible 0/+1



Table 1. Electrochemical Potentials^a for 1 and 3

	$E_{1/2} (-1/0)^b$	$E_{1/2} (0/+1)^b$	E_{cell}^{c}
$1 \ (\mathbf{R}_2 = \mathbf{Cl})^d$	-0.835	0.005	0.84
$1 \ (\mathbf{R}_2 = \mathbf{M}\mathbf{e})^e$	-0.940^{f}	-0.136	0.80^{h}
$1 \ (\mathbf{R}_2 = \mathbf{P}\mathbf{h})^e$	-0.956	-0.104	0.85
3a (R = Cl)	-0.481^{f}	0.195 (0.158) ^g	0.64^{h}
3b (R = Me)	-0.557^{f}	$0.073 (0.042)^g$	0.59^{h}
3c (R = Ph)	-0.529^{f}	$0.108 (0.071)^g$	0.60^{h}

^{*a*}Volts, in MeCN. ^{*b*}Reference to SCE. ^{*c*}E_{cell} = $|E_{1/2}(0/+1) - E_{1/2}(-1/0)|$. ^{*d*}R₁ = Me, see ref 9b. ^{*e*}R₁ = Me, see ref 9d. ^{*f*}Irreversible reduction, only the cathodic peak potential E_{pc} is cited. ^{*s*}E_{1/2} and E_{pc} (in parentheses). ^{*h*}E_{cell} estimated as $|E_{pc}(0/+1) - E_{pc}(-1/0)|$.

couple of 3a, 3b, and 3c which reflect the electron-withdrawing power of the axial ligand R; similar trends are observed for derivatives of [1].^{9b,d} Also provided in Table 1 is a comparison of the cell potentials E_{cell} for 1 and 3. In those cases where the -1/0 couple is irreversible the magnitude of E_{cell} has been estimated in terms of the difference in the E_{pc} values for the -1/0 and 0/+1 couples. Collectively, the low E_{cell} values observed for the oxobenzene-bridged radicals augur well for improved charge transport in these materials.

Based on the electrochemical data we selected octamethylferrocene OMFc ($E_{1/2}(\text{ox}) = -0.038 \text{ V vs SCE}$)^{12b,20} as a suitable reagent to convert [**3b**][OTf] to the corresponding radical **3b**, and subsequent bulk reduction of [**3b**][OTf] with OMFc was certainly effective in producing quantities of microcrystalline radical sufficient for magnetic and conductivity measurements. While slow codiffusion of MeCN solutions of OMFc and [**3b**][OTf] in a glass H-cell also produced predominantly microcrystalline material, a few crystalline shards of **3b** suitable for single crystal X-ray diffraction work were isolated. Powder diffraction analysis of the bulk microcrystalline material confirmed a structural match and phase uniformity.

Crystallography. The structural information for **3b** originates from a single crystal gleaned from a codiffusion (H-cell) reduction. Table 2 lists crystal data, while Figure 2 illustrates ORTEP drawings of the two radicals in the asymmetric unit, and provides the atom numbering scheme. Intramolecular distances and angles are all normal for radicals of this type; intermolecular S…O', S…N', and S…S' contacts are listed in Table 3. As noted above, the structure and phase purity of the bulk material was confirmed by powder diffraction methods; the results of a Rietveld refinement performed in GSAS are illustrated in Figure 3.²¹

Crystals of **3b** belong to the monoclinic space group C2/c, with Z = 8. There are 1 1/2 molecules in the asymmetric unit (Figure 2), with the **B** radicals occupying special positions,

Table 2. Crystal Data for 3b

formula	C_{10} $_{5}H_{4}$ $_{5}N_{3}O_{1}$ $_{5}S_{6}$
М	389.03
<i>a,</i> Å	25.828(3)
<i>b,</i> Å	14.5799(14)
<i>c,</i> Å	7.3586(7)
β , deg	95.687(2)
<i>V</i> , Å ³	2757.4(5)
$ ho_{ m calcd}~(m g~ m cm^{-1})$	1.871
space group	C2/c
Z	8
temp (K)	296(2)
$\mu (\mathrm{mm}^{-1})$	0.993
λ (Å)	0.71073
data/restraints/params	4020/0/192
solution method	direct methods
$R, R_{\rm w} $ (on F^2)	0.0582, 0.0774



Figure 2. ORTEP drawing (50% probability ellipsoids) of the two molecules (A and B) associated with the asymmetric unit of 3b, showing atom numbering schemes. Molecule B is bisected by a 2-fold rotation axis.

Table 3. Intermolecular Contacts^a

d1	S3a…O1b′	2.974		
d2	O1a…S1b′	3.131		
d3	S3a…N1b′	3.244		
d4	N1a…S1b′	3.101		
d5	S2a…S1b′	3.584		
d6	S2b…S1b′	3.710		
d7	S3a····S2a'	3.761		
d8	N2a…S1a'	3.165		
d9	O1a…S1a′	2.975		
d10	O1a…S2a′	2.968		
d11	S1a····S2a'	3.722		
^a Distances in Å; see Figures 4 and 5 for definitions of d1-d11.				

bisected by the 2-fold rotation axes parallel to the *b*-axis at x = 0, 1/2. The **A** radicals are located in general positions. The unit cell drawing shown in Figure 4 illustrates the packing of the radicals viewed parallel to the *c*-axis, and highlights the zigzag arrays of **A** radicals generated by the 2-fold screw axes at x = 1/4 and 3/4. The **B** radicals at x = 0, 1/2 are nested in the pockets formed by the out-of-register ribbons of **A**, and locked in place by a complex network of intermolecular S…S', S…O', and S…N' contacts d1-d5, all of which are within the respective van der Waals separation.²² There is also a set of short S…O', and S…N' interactions (d8-d10) which serve as structure-making links along the zigzag, ribbon-like arrays of **A**-radicals (Figure 5).

Both the **A** and **B** molecules form bases for alternating, but evenly spaced π -stacks, as illustrated in Figures 4 and 5. The head-over-tail overlay of the **B** radicals along the π -stacks is



Figure 3. Observed and calculated powder X-ray diffraction patterns for 3b ($\lambda = 1.5406$ Å).



Figure 4. Packing of radicals in the unit cell of **3b**, viewed parallel to the *c* axis (above). Alternation of radicals along the **A** and **B** π -stacks is shown below. The **B** radicals lie on a 2-fold rotation axis, and the methyl protons are disordered. Intermolecular S…S' (blue), S…O'(red), and S…N' (green) contacts are shown with dashed lines.

centrosymmetric, an arrangement which gives rise to a pair of intermolecular S…S' contacts d6. By contrast, the overlay of radicals along the π -stacks of **A** is less symmetric, and the orientation of consecutive radicals is rotated by an angle of 89.8°. As a result there are no short S…S' interactions save for that afforded by the rather oblique contact d7. The interplanar separation δ (3.413 Å) is nonetheless quite close; by contrast, in the **B** radical π -stacks, $\delta = 3.627$ Å. Overall, the perfect head-



Figure 5. Ribbons of **A** radicals running parallel to *b* (above) and skewed π -stacking of **A** radicals (below); alternate layers are interconverted by a 2-fold screw axis. Intermolecular S···S' (blue), S···O' (red), and S···N' (green) contacts are shown with dashed lines.

over-tail stacking adopted by the **B** radicals of **3b** is reminiscent of that found in the phenyl-substituted oxobenzene-bridged derivative **3c** (Figure 6),¹⁸ while the twisted packing of π -stacks



Figure 6. Alternating π -stacked architectures in 3c (ref 18) and 2a (at 295 K, ref 14), with intermolecular S…S' (blue) contacts shown with dashed lines.

found for the **A** radicals is more reminiscent of the architecture found in the *N*-methyl pyrazine-bridged radical 2a.¹⁴ It should be noted, however, that in 2a the mean planes of the radicals are (at 295 K) rigorously perpendicular to the stacking direction, whereas the **A** radicals in 3b are inclined by 68.1° to the *c*-axis.

An additional feature associated with the packing of the A radicals in **3b** is the *trans*-antarafacial, four-center interaction generated by the centrosymmetric approach of radicals in adjacent π -stacks. While the associated S…S' intermolecular distance (d11 = 3.722 Å) is nominally outside the van der Waals separation,²² the magnetic and electronic consequences of these interactions are of considerable importance; these effects are discussed below.

Magnetic Measurements. Variable temperature DC magnetic susceptibility (χ) measurements on **3b** have been carried out over the temperature range 2–300 K. The results are illustrated in Figure 7 in the form of cooling curve plots of χ



Figure 7. Field-cooled χ versus *T* (left) and χT versus *T* (right) plots for **3b** at *H* = 1 kOe.

and χT versus *T*, measured using an external field of *H* = 1 kOe. Inspection of the χT versus T plot suggests a strongly antiferromagnetic (AFM) response, since for a paramagnetic S = 1/2 system with a nominal value of $g \approx 2$ the high temperature limit of χT should fall near 0.375 emu K mol⁻¹. In this case, χT at 300 K is near 0.20 emu K mol⁻¹. Not surprisingly, attempts to perform even a Curie-Weiss fit to the high temperature data were unsuccessful, a finding that we attribute to the fact that the crystal structure contains two different S = 1/2 sublattices, one based on A radicals, with eight spins per cell, and the other composed of B radicals, with four spins per cell. In addition, the large number of close intermolecular contacts between pairs of A radicals, pairs of B radicals, and hybrid A/B pairs suggests a complex array of magnetic interactions, and an overall magnetic structure which is unlikely to conform to a simple description based on a 1D- or 2D-magnetic (chain or ladder) model, let alone follow Curie-Weiss behavior.

That being said, a qualitative understanding of the dominant magnetic interactions in 3b can be reached by using DFT calculations to estimate pairwise exchange energies J between radicals in the A and B π -stacks, that is, the values of J_1 , J_2 , and J_3 shown in Figure 8. These three dimers are defined respectively by the close contacts d11, d7 and d6 in Figures 4 and 5. On the basis of previous experience,^{11c} it is these π stack interactions, rather than those involving lateral interstack approaches, that are most likely to produce a strong antiferromagnetic response. The computational approach, which has been successfully applied to a variety of nitrogen-centered radicals,²³ heterocyclic thiazyls^{24,25} and phenalenyls,²⁶ employs exchange energies estimated using the broken symmetry DFT methods developed by Noodleman and Yamaguchi.²⁷ Accordingly, the exchange energy J for any pair of interacting radicals, defined with reference to the Heisenberg Hamiltonian $H_{\text{ex}} = -2J\{S_1 \cdot S_2\}$, can be derived from the total



Figure 8. Pairwise magnetic exchange interactions within the π -stacks of the **A** and **B** radicals in **3b**, with corresponding DFT estimated exchange energies J_1 , J_2 , and J_3 .

energies of the triplet $(E_{\rm TS})$ and broken symmetry singlet $(E_{\rm BSS})$ states and their respective expectation values $\langle S^2 \rangle$, according to eq 1. Single point total energies $E_{\rm TS}$ and $E_{\rm BSS}$ were calculated using the hybrid exchange correlation functional UB3LYP and polarized, split-valence basis sets with double- ζ (6-31G(d,p)) functions. Atomic coordinates were taken from the crystallographic data.

$$J = \frac{-(E_{\rm TS} - E_{\rm BSS})}{\langle S^2 \rangle_{\rm TS} - \langle S^2 \rangle_{\rm BSS}}$$
(1)

The numerical results given in Figure 8 indicate a large negative (AFM) J_1 value, suggesting an isolated open-shell singlet state for these dimers. By contrast the small, albeit positive value for J_2 indicates a 1D ferromagnetic interaction along the π -stacks of the **A** radicals. Finally, while the value of J_3 found for the π -stacks of the **B** radicals is smaller than that of J_1 , it is clearly large enough to suggest a well-developed 1D AFM chain interaction.²⁸ Of course, these conclusions exclude the cumulative effects of lateral interstack interactions, which are likely to further enrich the magnetic description. The present results nonetheless establish the presence of strong AFM magnetic responses within both the **A** and **B** π -stacks, the largest arising from the *trans*-antarafacial approach characterized by J_1 .

The *N*-methyl pyrazine-bridged radical 2a,¹⁴ which displays a similar alternating π -stack architecture (Figure 6), also possesses four-center, *trans*-antarafacial interactions (Figure 9a) akin to that found in **3b**. The S…S' separations (3.831 Å) are comparable to those found in **3b** (d11 = 3.722 Å), and the



Figure 9. Centrosymmetric four-center S···S' contacts in (a) the pyrazine-bridged bisdithiazolyl **2a** (ref 14), (b) *m*-cyanophenyl-dithiadiazolyl (ref 31), and (c) $[S_3N_2][AsF_6]$ (ref 32). For **2a** the estimated exchange energy **J** is also provided.

associated exchange energy $(J = -108.4 \text{ cm}^{-1})^{29}$ is even more negative, a finding which may provide an explanation for the strong AFM response observed for 2a.³⁰ However, the magnitude of these exchange interactions falls far short of those seen in more localized radical dimers, such as the centrosymmetrically bridged *m*-cyanophenyl-dithiadiazolyl³¹ and many salts of the binary cation S₃N₂⁺, including [S₃N₂][AsF₆].³² In these latter systems (Figures 9b and 9c) the S…S' bridges are much shorter, so that the electronic structures of the dimers should no longer be considered as open shell singlets,³³ but rather as a closed shell singlets best described in terms of a classical 4-center 2-electron bond model.³⁴

Conductivity. Variable temperature conductivity (σ) measurements on the oxobenzene-bridged radicals **3a**, its acetonitrile adduct **3a**·MeCN, and **3c** were reported in earlier work.^{17,18} Similar experiments on **3b**, using the four-probe method on cold-pressed pellets, have now been performed. The results for all four compounds are illustrated in Figure 10, in the



Figure 10. Plots of log σ versus 1/T for oxobenzene-bridged radicals. Derived thermal activation energies are listed in Table 4. Data for **3a**, **3a**·MeCN, and **3c** are from refs 17 and 18.

form of log plots of σ against 1/*T*; values of σ (300 K) and the Arrhenius activation energy E_{act} are summarized in Table 4.

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	3a·MeCN ^a	3a ^a	3b	$3c^b$
$\sigma(300 \text{ K}) \ (\text{S cm}^{-1})$	3.0×10^{-3}	4.0×10^{-3}	9.0×10^{-4}	3.0×10^{-5}
$E_{\rm act}~({\rm eV})$	0.11	0.16	0.13	0.20
^a Ref 17. ^b Ref 18				

While there are variations within the group 3a, 3a·MeCN, 3b, and 3c, their collective performance is markedly and uniformly superior to that of related pyridine-bridged materials, both in terms of enhanced conductivity and lowered activation energy. Indeed the values of $\sigma(300 \text{ K})$ are comparable to those found in selenium-based variants of 1.¹¹ Moreover, while the conductivity of 3b is activated, indicative of a Mott insulating ground state, the value of $E_{act} = 0.13 \text{ eV}$ is second only to that found for 3a·MeCN, a material which, to our knowledge, displays the lowest thermal activation energy ever reported for a neutral f = 1/2 radical.¹⁷

Band Structure Calculations. To explore the electronic structure of 3b we have carried out a series of EHT band structure calculations based on the crystal structure geometry.

Crystal Growth & Design

As with the results obtained for other oxobenzene-bridged materials¹⁷ the numerical data must be viewed with caution, as for strongly correlated Mott insulating systems such as these the tight-binding approximation fails to provide a proper description of the ground state. The method nonetheless provides qualitative insight into the direction and extent of intermolecular orbital interactions within and between the radical π -stacks. As in the case of **3a** and **3c**, we focus on the dispersion of the singly occupied molecular orbitals (SOMOs) on neighboring molecules along and between the radical π -stacks. Idealized views of this antibonding A₂ symmetry orbital are illustrated in Figure 11.



Figure 11. Idealized views of the $A_2 \pi$ -SOMO of 3b.

Given the unusual nature of the crystal structure, that is, the presence of two distinct sublattices, we have performed calculations on several idealized structures, the first based on a single ribbon of **A** radicals, π -stacked along the *z* direction and running parallel to *y*, as shown in Figure 5. The second model addresses the full 3D sublattice of **A** radicals, the honeycomb nature of which is illustrated by the space-filling superstructure in Figure 12. The effects of the inclusion of the sublattice of **B**



Figure 12. Two sublattices of 3b, viewed parallel to the stacking direction, with B radicals occupying cavities generated between out-of-register ribbons of A radicals.

radicals is then considered as a perturbation of the electronic structure of the A sublattice.

The results of the band structure calculations are summarized in Figure 13 in the form of dispersion curves along the direction $\Gamma \rightarrow Z$ for the SOMO-based COs,³⁵ which collectively would constitute the f = 1/2 band if the ground state were metallic. Inasmuch as the number of bands reflects the number of molecules in the unit cell, there are (i) four bands in the 2D lattice based on A radicals, (ii) eight bands for the full 3D lattice of A radicals, and (iii) twelve bands (8A + 4B) for the full 3Dlattice based on both radicals A and B. As may be seen in Figure 13(i) the four COs are split into two pairs, an effect which can be traced back to the influence of the *trans*-antarafacial overlap



Figure 13. EHT band structure of different models of **3b**, showing (i) CO dispersion of a 2D array (along y and z) of **A** radicals, (ii) a full 3D set of **A** radicals, and (iii) the full 3D structure with **A** and **B** radicals.

(d11, Figure 5), which gives rise to the strong AFM exchange interactions J_1 . Nominally, and again speaking within the limits of the EHT method, this weak dimerization generates a very small band gap. On moving from the 2D to 3D lattice of **A** radicals, as in Figure 13(ii), the band gap almost closes, as might be expected from the increase in dimensionality. Finally, when the cavities in the superstructure of **A** radicals are filled with π -stacks of **B** radicals (Figure 13(iii)), a continuum of COs is generated, giving rise to an overall bandwidth W = 0.48 eV. That being said, the orbital interactions between the **A** and **B** radical π -stacks do not appear to be extensive, so that to a first approximation it is tempting to describe the overall structure in terms of two separate sublattices (**A** and **B**), with the former possessing stronger electronic interactions.

DISCUSSION AND CONCLUSION

The use of secondary bonding interactions³⁶ or supramolecular synthons¹⁶ to influence if not control the solid state structure of thiazyl radicals has a long history. For example, the role of nitrile CN···S^{'31,37} and covalent F···S^{'38} contacts to control supramolecular architecture, and four-center (S···N')₂ interactions to generate centrosymmetric pairings,³⁹ has been well recognized. More recently, the importance of intermolecular carbonyl CO···S contacts, both in thiazyl chemistry^{17,18,40} and elsewhere,¹⁵ has also been noted. In this light the concerted effect of chelating S···O' and S···N' interactions to lock adjacent radicals into 1D ribbon-like arrays (Figure 14), is not surprising. In the case of **3a**·MeCN, these ribbons are packed into slipped π -stacks (Figure 1c) which afford a large electronic bandwidth and correspondingly high conductivity.¹⁷ The crystal structure of **3b** described here is more complex, in that it is bimodal, with two completely different radical environments. One of these



Figure 14. Ribbon-like arrays of radicals created by intermolecular $S \cdots O'$ and $S \cdots N'$ supramolecular synthons.

radicals (**A**) adopts a ribbon-like structure akin to that found in $3a \cdot MeCN$, but consecutive ribbons along the stacking direction are now related by a 2-fold screw axis rather than a translation, an effect which leads to a doubling of the cell dimension. The out-of-register packing of these 1D arrays of **A** radicals affords an open 2D framework, a pseudoporous superstructure, within which π -stacked columns of **B** radicals are sequestered (Figure 12).

Bimodal radicals are rare. Indeed to our knowledge 3a, with three molecules in the asymmetric unit, is the only other radicalbased material known to exist with more than one crystallographically distinct site. That being said there are a number of reports of dithiadiazolyl and dithiazolyl radicals with two distinct radical environments, but in these systems at least one of the two radicals is dimerized, as a result of which there is no question of magnetic communication between the two sites.⁴¹ Rawson has reported a dimer formed by association of two chemically different dithiadiazolyls,⁴² but again in the absence of unpaired spins there is no magnetic manifestation of the presence of different building blocks. Likewise examples of radicals doped into host structures are rare. The incorporation of thiazyl radicals into a variety of diamagnetic hosts, both organic and inorganic, has been described, in all cases affording materials in which the paramagnetic centers are essentially isolated.43 There is also an example of a verdazyl radical clathrate in which the radicals are locked into columnar arrays, an arrangement which gives rise to strong AFM coupling along the π -stacks (as observed here).⁴⁴ More recently Pöppl has shown that nitronyl nitroxides incorporated into a copper framework $Cu_3(btc)_2$ (btc = benzenetricarboxylic acid) modify the magnetic properties of the host lattice.⁴⁵ In the case of 3b the extent of magnetic communication between the two sublattices is difficult to assess, as strong AFM coupling is anticipated in both.

In regard to the charge transport properties of **3b**, the question arises as to the origin of its high conductivity and low thermal activation energy. The electrochemical evidence suggests an intrinsically low *U* for oxobenzene-bridged radicals in general, and the π -stacked slipped ribbon architecture previously described for **3a**·MeCN clearly provided a significant enhancement in bandwidth (W = 1.02 eV). In that light, the performance of the unsolvated chloro radical **3a** and the methyl radical **3b** is perplexing, as the results of the EHT calculations for both suggest somewhat weaker electronic interactions than those seen in **3a**·MeCN.¹⁷ Indeed the values of *W* estimated for **3a** (0.52 eV) and **3b** (0.48 eV) are comparable to that found for the highly one-dimensional, and less conductive, phenyl-substituted material **3c** (W = 0.49 eV).⁴⁶

This seemingly anomalous performance of 3a and 3b, both of which display high conductivity and low excitation energies in spite of a relatively low bandwidth, may be related to the fact that they are bi- (or tri-) modal. The different electronic environments (crystal fields) experienced by the crystallographically distinct radicals may give rise to subtle differences in their individual electronic properties, which would be manifest in their ion energetics (IP and EA values), effects that are not registered in the EHT calculations. In essence charge transport in 3b (and 3a) may be aided by a form of self-doping, a phenomenon which has been observed for heterostructures formed at the interfaces between inorganic oxide Mott insulators.⁴⁷ For these latter systems it has been shown that charge transfer at the surface can lead to significant improvements in conductivity, even to the generation of metallic states. In the present case the degree of doping, charge transfer between the **A** and **B** sites, is likely to be very small, but may be sufficient to improve charge transport. Testing these ideas, by making materials with *crystallographically* distinct radical centers, is a nontrivial task. It would, however, be relatively easy to generate bimodal materials with two *chemically* distinct f = 1/2 building blocks, either by cocrystallization techniques⁴⁸ or by using mixed biradicals.⁴⁹ Charge polarization in such systems could lead to a smaller, possibly vanishing, Mott–Hubbard gap.

EXPERIMENTAL SECTION

General Methods and Procedures. The reagents sulfur monochloride, octamethylferrocene (OMFc), silver triflate (trifluoromethanesulfonate) and 2,6-dinitro-p-cresol 4 were obtained commercially. All were used as received save for OMFc, which was sublimed in vacuo and recrystallized from acetonitrile before use. The solvents acetonitrile (MeCN), dichloroethane (DCE), dichloromethane (DCM) and carbon disulfide were of at least reagent grade. MeCN was dried by distillation from P₂O₅ and CaH₂, and both DCE and DCM by distillation from P2O5. All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. Infrared spectra (Nujol mulls, KBr optics) were recorded on a Nicolet Avatar FTIR spectrometer at 2 cm⁻¹ resolution, and visible spectra were collected on samples dissolved in MeCN using a Perkin-Elmer Lambda 35 UV-vis spectrophotometer. ¹H NMR spectra were run on a Bruker Avance 300 MHz NMR spectrometer and low resolution Electro-Spray Ionization (ESI) mass spectra were recorded on a Micromass Q-TOF Ultima Global LC/MS/MS system. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ 85018.

Preparation of 2,6-Diamino-4-methylphenol Bishydrochloride 5. Following the procedure described for 2,6-diaminophenol,⁵⁰ tin powder (12.7 g, 0.107 mol) was added in three portions to a suspension of 2,6-dinitro-p-cresol 4 (5.5 g, 27.7 mmol) in 50 mL of concentrated HCl at 0 °C. When effervescence had ceased the mixture was allowed to warm to room temperature, then filtered through glass wool and the solvent removed from the filtrate by flash evaporation. The remaining solid was washed with 10–15 mL of concentrated HCl, then redissolved in 10-15 mL of deionized water to give a pale yellow solution. HCl gas was slowly bubbled through the solution for ~ 15 min until the white crystalline product 5 formed. This material was collected by filtration and air-dried. A second, smaller portion of 5 crystallized from the filtrate and was also collected by filtration. Total yield 5.00 g (23.7 mmol, 85%); mp >250 °C. ¹H NMR (DMSO) δ : 2.11 (s, 3H), 6.05 (s, 2H).⁵¹Anal. Calcd. for C₇H₁₂N₂OCl₂: C, 39.83; H, 5.73; N, 13.27. Found: C, 40.01; H, 5.61; N, 13.41.

Preparation of [3b][Cl]. Sulfur monochloride (16 mL, 27.0 g, 200 mmol) was added dropwise to a solution of 4-methyl-2,6-diaminophenol bishydrochloride **5** (4.33 g, 19.9 mmol) in 250 mL anhydrous MeCN, and the mixture was heated under gentle reflux overnight. The purple-brown precipitate of [**3b**][Cl] was filtered off, washed thoroughly with MeCN and dried in vacuo. Yield 5.22 g (17.1 mmol, 89%); mp >250 °C. IR (cm⁻¹): 1669 (s), 1406 (s), 1583 (s), 1090 (w), 1002 (m), 950 (w), 913 (w), 846 (m), 783 (w), 756 (s), 656 (w), 489 (m), 471 (w).

Preparation of [3b][OTf]. Silver triflate (2.89 g, 11.2 mmol) was added to a slurry of crude [**3b**][Cl] (2.96 g, 10.0 mmol) in 150 mL anhydrous MeCN, to afford a deep purple solution, which was gently heated at reflux for 1 h, then filtered to remove a gray precipitate of AgCl. The solvent was flash distilled from the filtrate to leave crude product as a dark red solid (3.86 g), which was recrystallized from hot MeCN to give metallic green shards of [**3b**][OTf] (2.51 g, 6.15 mmol, 61%); mp >250 °C. Anal. Calcd. for $C_8H_3F_3N_2O_4S_5$: C, 23.52; H, 0.74; N, 6.86. Found: C, 23.36; H, 0.91; N, 7.00. IR (cm⁻¹): 1683 (s), 1409 (s), 1288 (s), 1270 (s), 1238 (s), 1159 (s), 1030 (s), 1006 (m), 853 (w), 762 (s), 660 (m), 638 (s), 660 (m), 938 (s), 573(w), 515

Crystal Growth & Design

Preparation of 3b. Method 1. Bulk Material for Conductivity and Magnetic Measurements. A solution of [3b][OTf] (250 mg, 0.613 mmol) in 75 mL of degassed MeCN (3 freeze-pumpthaw cycles) was filtered into a solution of OMFc (210 mg, 0.944 mmol) in 175 mL of similarly degassed MeCN to yield a blue solution and a blue-black precipitate. After 1 h of stirring at room temperature, the purple microcrystalline product was filtered off, washed with MeCN and dried under vacuum, (69 mg, 0.266 mmol, 43% yield); mp >250 °C. Anal. Calcd. for $C_7H_3N_2OS_4$: C, 32.41; H, 1.17; N, 10.80. Found: C, 32.46; H, 1.17; N, 10.96. IR (cm⁻¹): 1575 (s, br), 1456 (s), 1377 (s), 1285 (s, br), 1134 (w), 1029 (w), 1066 (w), 825 (w), 768 (w), 727 (m), 681 (m), 634 (m), 503 (w), 471 (w), 438 (w).

Method 2. Slow Diffusion for Single Crystals. A solution of [3b][OTf] (75 mg, 0.184 mmol) in 15 mL degassed (4 freezepump-thaw cycles) MeCN was allowed to diffuse slowly into a similarly degassed solution of OMFc (64 mg, 0.221 mmol) over a 6 h period, affording 3b as microcrystalline solid with a few single crystals which were manually separated for single crystal work.

Cyclic Voltammetry. Cyclic voltammetry was performed using a PINE Bipotentiostat, Model AFCClBP1, with scan rates of 50–250 mV s⁻¹ on solutions of [**3b**][OTf] in MeCN (dried by distillation from P_2O_5 and CaH₂) containing 0.1 M tetra-*n*-butyl-ammonium hexafluorophosphate. Potentials were scanned with respect to the quasi-reference electrode in a single compartment cell fitted with Pt electrodes and referenced to the Fc/Fc⁺ couple of ferrocene at 0.38 V vs SCE. The $E_{\rm pa}$ - $E_{\rm pc}$ separation of the reversible couples were within 10% of that of the Fc/Fc⁺ couple.⁵²

Crystallography. Crystals were glued to glass fibers with epoxy. Xray data for 3b were collected using omega scans with a Bruker APEX I CCD detector on a D8 3-circle goniometer and Mo K_a ($\lambda = 0.71073$ A) radiation. The data were scanned using Bruker's SMART program and integrated using Bruker's SAINT software.⁵³ The structures were solved by direct methods using SHELXS-90⁵⁴ and refined by leastsquares methods on F^2 using SHELXL-97⁵⁵ incorporated in the SHELXTL⁵⁶ suite of programs. Powder X-ray diffraction data on bulk **3b** were collected at ambient temperature on a powder diffractometer equipped with a position sensitive detector (INEL) using Cu K_{a1} radiation ($\lambda = 1.5406$ A°). The total 2 θ range was 0–112°, measured in steps of 0.029°. Starting with the space group, unit cell and the molecular coordinates available from the single crystal data set, the unit cell dimensions were refined by Rietveld methods⁵⁷ using the GSAS program package.⁵⁸

Magnetic Susceptibility Measurements. DC magnetic susceptibility measurements on **3b** were performed over the temperature range 2–300 K on a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants.⁵⁹

Conductivity Measurements. Four-probe temperature dependent conductivity measurements on cold pressed pellet $(1 \times 1 \times 5 \text{ mm})$ samples of **3b** were performed over the range 140–300 K using homebuilt equipment. Silver paint (Leitsilber 200) was used to apply the electrical contacts.

Band Structure Calculations. EHT Band electronic structure calculations were performed with the Caesar 2.0 suite of programs⁶⁰ using the Coulomb parameters of Baasch, Viste and Gray⁶¹ and a quasi-split valence basis set adapted from Clementi and Roetti.⁶² The off-diagonal elements of the Hamiltonian matrix were calculated with the standard weighting formula.⁶³ Atomic positions were taken from crystallographic data.

Exchange Energy Calculations. All calculations were performed using the UB3LYP functional and the split-valence double- ζ basis set 6-31G(d,p), as contained in the Gaussian 09W suite of programs.⁶⁴ Exchange energies J_1 , J_2 , and J_3 for interacting pairs of radicals in **3b** were computed from eq 1, using single point energies of the triplet and broken symmetry singlet states and their respective $\langle S^2 \rangle$ expectation values. Tight convergence criteria were employed, and atomic coordinates were taken from crystallographic data.

ASSOCIATED CONTENT

Supporting Information

Details of single crystal X-ray crystallographic data collection and structure refinement, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions in CIF format. Archival files for DFT calculations of magnetic exchange energies. This information 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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(29) This value was calculated using equation 1, at the same level of theory as for $J_{1,2,3}$, and with atomic coordinates taken from the reported crystal structure.

(30) There is also a noncentrosymmetric four-center interaction in 2a. At 295 K, the two S…S'distances are longer (3.936 and 4.093 Å), but the calculated exchange energy ($J = -61.1 \text{ cm}^{-1}$) indicates an even stronger AFM response.

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