Electronic Supporting Information

Supramolecular architecture, crystal structure and transport properties of the prototypal oxobenzene-bridged bisdithiazolyl radical conductor

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Contents

Section 1 Synthetic Procedures

General Methods. The reagents thionyl chloride, elemental bromine and tin, ammonium thiocyanate, octamethylferrocence (OMFc) were obtained commercially. Silver nonoafluorobutane-sulfonate (AgONf) was prepared according to literature methods.[1] 2,6-Diaminoanisole **2** was prepared by reduction of 2-methoxy-1,3-dinitrobenzene,[2] itself prepared by treatment of 2-chloro-1,3-dinitrobenzene with sodium methoxide (both obtained commercially).[3] The solvents acetonitrile (MeCN), propionitrile (EtCN), dichloroethane (DCE), dichloromethane (DCM), carbon disulfide, hexane and diethyl ether were of at least reagent grade. MeCN and EtCN[4] were dried by distillation from P_2O_5 and CaH_2, and DCM by distillation from P_2O_5. 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-Diamineanisole-3,5-dithiocyanuric ester 3. 2,6-Diaminoanisole **2** (2.50 g, 18.1 mmol) and ammonium thiocyanate (11.0 g, 14.4 mol) was dissolved in 150 mL MeOH at 0 °C. A solution of Br_2 (3.75 mL, 14.6 mmol) in 20 mL MeOHwas added dropwise over 30 min to give a cream colored precipitate. The mixture was stirred at 0 °C for one h, then poured onto 100 mL crushed ice and the cream colored precipitate was collected by filtration. Recrystallization from

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[1] M. Frasch, W. Sundermeyer and J Waldi, *Chem. Ber.* 1992, **125**, 1763.

[2] N. J. Clecak, S. Jose, R. J. Cox, L. Gatos, S. L. Solar, S. Jose and H. K. Wurster, *US Patent,* 3489558 (1970).

[3] A. Banerjee and I. N. Ngwendson, *US Patent*, 20070179311 A1 (2007).

[4] C. L. L. Chai and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 5th Ed.; Butterwirth-Heinemann: New York, 2003.

EtOH afforded lustrous cream needles of **3**, yield 3.20 g (1.28 mmol, 70%), mp: 153-156 °C; IR: 3475 (w), 3429 (w), 3374 (w), 3322 (w), 2358 (w), 2151 (w), 1608 (m), 1235 (w), 992 (w), 721 (w) cm^{-1}. ^{1}H NMR (δ, C_6D_6): 6.72 (s, 1H, Ar-H), 3.89 (s, 2H, NH_2), 2.91 (s, 3H, $-OCH_3$). Anal. Calcd for $C_9H_8N_4OS_2$: C, 42.84; H, 3.20; N, 22.21. Found: C, 42.73; H, 3.34; N, 22.07.

Preparation of 2,6-diamino-3,5-anisole-2,5-dithiol 4. 2,6-Diaminoanisole-3,5-dithiocyanuric ester **3** (2.13 g, 8.43 mmol) and sodium sulfide nonahydrate (8.11 g, 33.8 mmol) were dissolved in 250 mL of degassed water and warmed to 60 °C under a flow of nitrogen. The mixture was hot filtered, cooled on an ice-water bath and acetic acid was added dropwise to pH ~ 6 to give a yellow precipitate which was filtered off, dried in vacuo and used in subsequent steps without further purification; yield 1.51 g (7.44 mmol, 89% yield); IR: 3401 (w), 2724 (w), 2508 (w), 1602 (m), 1217 (m), 1152 (w), 1030 (m), 872 (w), 722 (w) cm^{-1}. ^{1}H NMR (δ, C_6D_6): 7.49 (s, 1H, Ar-H), 4.01 (s, 2H, NH_2), 3.34 (s, 3H, $-OCH_3$), 2.49 (s, 1H, SH).

Preparation of [1a][Cl]. 2,6-Diamino-3,5-dithioanisole **4** (2.04 g, 10.1 mmol) was dissolved in 100 mL freshly distilled MeCN. Thionyl chloride (6.45 g, 54.2 mmol) was added dropwise to the yellow solution, which was heated a gentle reflux for 2 h. The dark purple precipitate was collected by filtration, washed with 20 mL MeCN, then refluxed with 20 mL of DCE, hot filtered and washed 2 × 20 mL DCM to give crude [**1a**][Cl] as a purple-black powder, yield 2.60 g (9.26 mmol, 92%). IR: 1657 (m), 1320 (s), 1046 (w), 1021 (w), 769 (w), 747 (w) cm^{-1}.

Preparation of [1a][ONf]. Crude [**1a**][Cl] (2.60 g, 9.26 mmol) was added to solution of silver nonafluorobutanesulfonate, AgONf (3.76 g, 9.23 mmol) in 100 mL of freshly distilled MeCN, and the mixture heated under gentle reflux for 30 min. The mixture was hot filtered and the solvent flashed distilled to leave a deep red solid. This solid was triturated with CH_2Cl_2:AcOH (10:1) and the dark purple precipitate so formed collected by filtration; crude yield 3.09 g (5.68 mmol, 61%). Subsequent recrystallization of this material from MeCN and EtCN afforded lustrous dark green shards of analytically pure [**1a**][ONf]; yield 1.54 g (2.83 mmol, 50% yield); mp: > 250 °C. IR: 1485 (s), 1467 (s), 1396 (m), 1327 (s), 1274 (s), 1223 (s), 1135 (s), 1058 (s), 766 (s), 657 (m) cm^{-1}. UV-vis: λ_{max} 554 nm, $\varepsilon = 1.5 \times 10^4$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{10}HF_9N_2O_4S_4$: C, 22.06; H, 0.19; N, 5.45. Found: C, 22.21; H, 0; N, 5.45.

Preparation of 1a. **Method 1. Bulk material for conductivity and magnetic measurements**. A solution of [**1a**][ONf] (450 mg, 0.827 mmol) in 120 mL of degassed (three freeze-pump-thaw cycles) MeCN was filtered into a stirred solution of OMFc (320 mg, 1.07 mmol) in 50 mL of similarly degassed MeCN, yielding a dark purple solution over a dark purple microcrystalline solid. After 1 h the product was filtered off, washed with 3 × 20 ml of dry MeCN, and dried *in vacuo*; yield 200 mg (0.815 mmol, 99%). IR: 3401 (w), 2724 (w), 2508 (w), 1602 (s), 1217 (m), 1152 (w), 1100 (w), 1030 (m), 938 (w), 872 (w),722 (w) cm^{-1}. Anal. Calcd for $C_6HN_2OS_4$: C, 29.37; H, 0.41; N, 11.42. Found: C, 29.30; H, 0.61; N, 11.25. **Method 2. Slow Diffusion for Single Crystals.** A solution of [**3a**][NOf] (54 mg, 0.99 mmol) in 13 mL degassed (4 freeze-pump-thaw cycles) MeCN was allowed to diffuse slowly into a similarly degassed solution of OMFc (60 mg, 2.01 mmol) over a 6 h period, affording **1a** as very fine, hairlike needles.

Section 2 Cyclic Voltammetry.

Cyclic voltammetry was performed using a PINE Bipotentiostat, Model AFCClBP1, with scan rates of 50-250 mV s^{-1} on solutions of [**1a**][OTf] in MeCN (dried by distillation from P_2O_5 and CaH_2) 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_{pa}-E_{pc} separation of the reversible couples were within 10 % of that of the Fc/Fc$^+$ couple.[5]

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[5] (a) R. T. Boeré, K. H. Moock and M. Parvez, *Z. Anorg. Allg. Chem.* 1994, **620**, 1589. (b) R. T. Boeré and T. L. Roemmele, *Coord. Chem Rev*. 2000, **210**, 369.

Section 3 Conductivity Measurements.

Four-probe temperature dependent conductivity measurements on cold pressed pellet (1×1×5 mm) samples of **1a** were performed over the range 140-300 K. A homemade device was used to measure the voltage drop under dynamic vacuum. Silver paint (Leitsilber 200) was used to apply the electrical contacts.

Section 4 Crystallography.

A single microcrystal of **1a** was mounted on a MiTeGen MicroMount using Fomblin oil. The data were measured on beamline I19 at the Diamond Light Source, collected using Rigaku CrystalClear software[6] and processed with Bruker APEX2 software[7] and SADABS[8] and OLEX2.[9] Final data: $C_6N_2HOS_4$, M = 245.33, black platelet, 0.120 × 0.010 × 0.002 mm, orthorhombic, space group *Fdd*2 (No. 43), $a = 27.876(3)$ Å, $b = 31.252(4)$ Å, $c = 4.0004(5)$ Å, $F_{000} = 1968$, $\lambda = 0.68890$ Å. $T = 296(2)$ K, $2\theta_{max} = 53.9°$, Flack parameter = 0.06(8), 1873 reflections, final GooF = 1.114, $R_1 = 0.0235$, wR_2 = 0.0.0524.

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[6] *CrystalClear*; Rigaku Corporation: Tokyo, Japan, 2005.

[7] *APEX2*; Bruker AXS Inc.: Madison, WI, 2007.

[8] *SADABS*; Bruker AXS Inc.: Madison, WI, 2001.

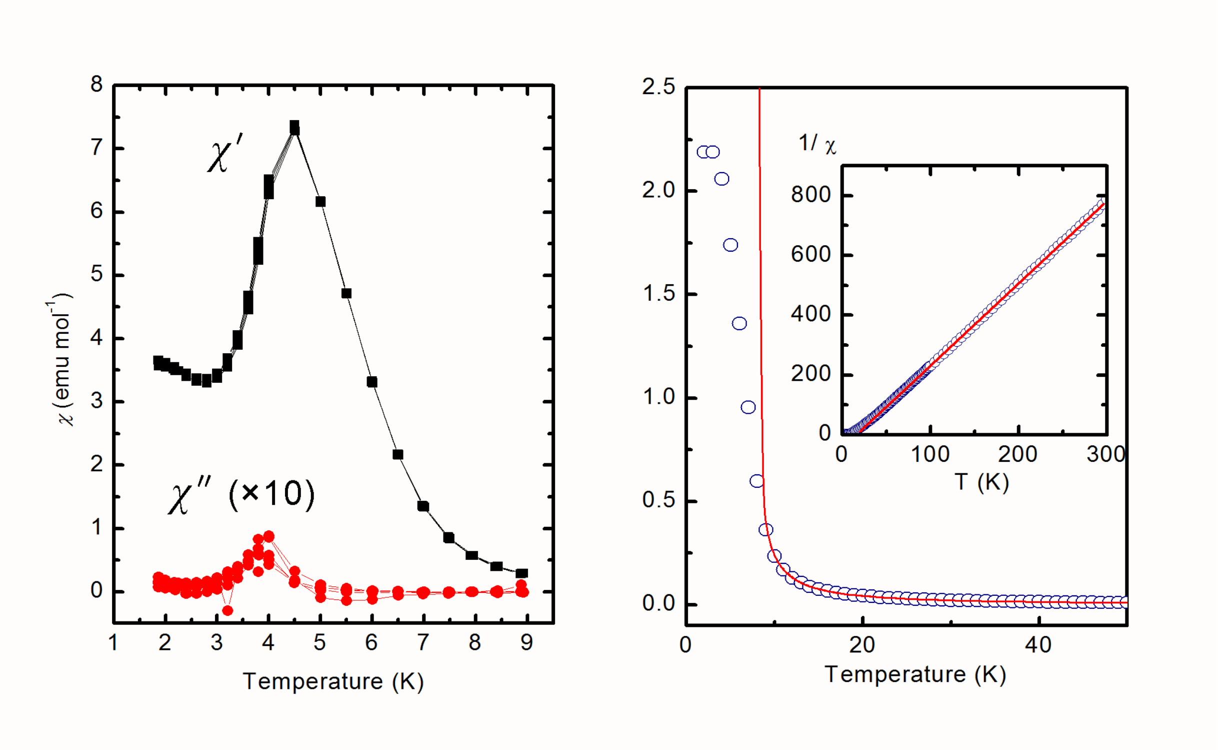
[9] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*., 2009, **42**, 339.

Table of Intermolecular Contacts (see Figure 2)

Atom1	**Atom2**	**Symm. op. 1**	**Symm. op. 2**	**Length (ESI)**
		Atom 1	**Atom 2**	**Angstroms**
C4	H4'	x, y, z	1/2-x, 1-y, -1/2+z	2.87(2)
H4	C4'	x, y, z	1/2-x, 1-y, 1/2+z	2.87(2)
N1	S3'	x, y, z	3/4-x, 1/4+y, -1/4+z	3.164(2)
N1	S4'	x, y, z	3/4-x, 1/4+y, -1/4+z	3.056(2)
O1	S1'	x, y, z	1/4+x, 1.25-y, -3/4+z	3.128(2)
O1	S2'	x, y, z	1/4+x, 1.25-y, -3/4+z	3.124(2)
O1	S3'	x, y, z	3/4-x, 1/4+y, -1/4+z	3.309(2)
S1	O1'	x, y, z	-1/4+x, 1.25-y, 3/4+z	3.128(2)
S2	S3'	x, y, z	1/2-x, 1-y, 1/2+z	3.540(1)
S2	O1'	x, y, z	-1/4+x, 1.25-y, 3/4+z	3.124(2)
S3	S2'	x, y, z	1/2-x, 1-y, -1/2+z	3.540(1)
S3	N1'	x, y, z	3/4-x, -1/4+y, 1/4+z	3.164(2)
S3	O1'	x, y, z	3/4-x, -1/4+y, 1/4+z	3.309(2)
S4	S4'	x, y, z	1-x, 1-y, z	3.486(1)
S4	N1'	x, y, z	3/4-x, -1/4+y, 1/4+z	3.056(2)

Section 5 Magnetic Susceptibility Measurements.

DC magnetic susceptibility measurements on **1a** were performed over the temperature range 2-300 K on a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants.[10] AC susceptibility measurements were obtained using a Quantum Design MPMS-XL7 SQUID magnetometer, with an oscillating AC field of 3 Oe, and AC frequencies ranging from 0.1-1500 Hz. An overlay of data recorded at 0.1, 1.0, 10, 100 and 1,000 Hz is shown below (left). The results of a Curie-Weiss fit to the 1000 Oe DC cooling curve from T = 30-300 K are shown below (right). This afforded C = 0.364 emu mol^{-1} and θ = +15.6 K.



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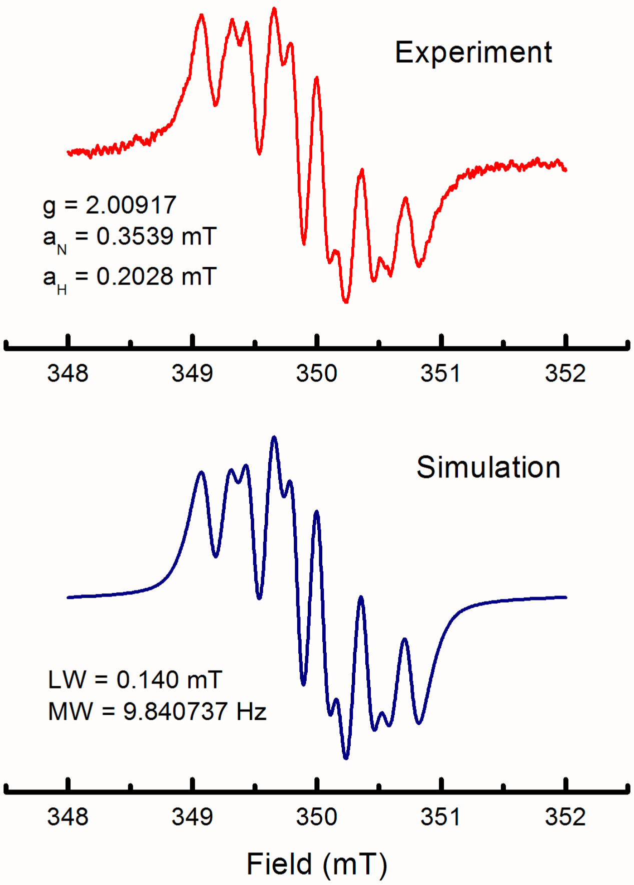
[10] Carlin, R. L. *Magnetochemistry*, Springer-Verlag, New York, 1986.

Section 6 Electron Paramagnetic Resonance Spectroscopy.

The X-band electron paramagnetic resonance (EPR) spectrum of **1a** was recorded at room temperature on a sample dissolved in degassed carbon disulfide (3 freeze-pump-thaw cycles), using a Bruker EMX spectrometer. Hyperfine coupling constants were obtained by spectral simulation using Simfonia and WinSim.[11]



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[11] *WinEPR Simfonia*; version 1.25; Bruker Instruments, Inc.: Billerica, MA, 1996.