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Research paper

A structurally-characterized zinc 2,5-diiminobenzoquinoid chain compound

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ABSTRACT

The incorporation of amino-substituted benzoquinoid bridging ligands into extended solids may provide a route to access light-weight metal-organic solids with high-temperature magnetic behavior and electronic conductivity. Reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with 2,5-diamino-3,6-dibromo-1,4-benzoquinone ($^{Br}LH_2$) in DMF at 130 °C gave a black crystalline solid of the compound $Zn(^{Br}L)(DMF)$, which features a structure comprised of one-dimensional chains made up of alternating Zn^{II} ions and $^{Br}L^{2-}$ bridging ligands. The preservation of NH groups on $^{Br}L^{2-}$ was confirmed by X-ray crystallography, a suite of spectroscopic measurements, and elemental analysis. To our knowledge, this chain compound represents the first structurally-characterized solid that contains amino-substituted benzoquinoid bridging ligands. Finally, an ambient temperature electronic conductivity value of $\sigma = 1.076(5) \times 10^{-12}\ S \cdot cm^{-1}$ was measured for the chain compound.

1. Introduction

Derivatives of 2,5-dihydroxy-1,4-benzoquinone have been extensively employed as bridging ligands in the formation of coordination compounds, spanning dinuclear molecular complexes [1] to extended solids of dimensionalities from one to three [2]. These ligands can direct the formation of metal compounds that display a wide range of interesting physical properties, owing largely to their ability to exist in both $S = 0$ benzoquinoid and $S = {}^1/_2$ semiquinoid form. In particular, dinuclear complexes of benzo- and semiquinoid ligands have been shown to exhibit unusual electronic and magnetic phenomena, such as valence tautomerism [3], optical switching [4], electron delocalization [5], and strong metal-semiquinoid magnetic coupling [6].

Despite the rich and diverse set of physical properties associated with the molecular benzoquinoid complexes noted above, the realization of analogous behavior in extended solids has been considerably more limited. Indeed, such solids may exhibit properties such as single-chain magnet behavior [7], bulk magnetic ordering [8], and electronic conductivity [9]. The relative lack of progress stems largely from the fact that semiquinoid radical bridging ligands derived from dihydroxy-substituted benzoquinone have only recently been incorporated into extended solids [10]. Nevertheless, these recent studies have shown that the resulting solids indeed demonstrate exceptional properties, including ferrimagnetic ordering up to 80 K [10a] and electronic conductivity values up to $0.16(1)\ S \cdot cm^{-1}$ [10a].

One route to metal semiquinoid solids with magnetic behavior at higher temperature and larger values of electronic conductivity is through substitution of some or all oxygen donor atoms on the bridging ligand with nitrogen atoms (see Scheme 1), owing to the better energetic overlap between nitrogen and transition metals relative to oxygen. Indeed, both benzoquinoid [11] and semiquinoid [6f,g] ligands that feature four nitrogen donors have been shown to exhibit much stronger metal-metal and metal-ligand radical coupling, respectively, than is observed in the oxygen-based analogues. Moreover, a copper solid derived from a hexaamino-substituted triphenylene ligand was shown to be 100-fold more electronically conductive than the analogous hexahydroxy-based compound [12], with its nickel analogue exhibiting one of the highest conductivity values reported for any metal-organic solid [13].

Despite this potential, to date no extended solid that incorporates an amino-substituted benzoquinoid bridging ligand has been structurally characterized. This is possibly due to a combination of two factors. First, replacing hydroxo with amino groups leads to an increase in pK_a, owing to the more electropositive nitrogen. The presence of these weakly acidic protons demands the use of strong bases during compound syntheses and gives rise to strong, irreversible bonding between metal ion and amido conjugate bases that can preclude the formation of crystalline products. In addition,

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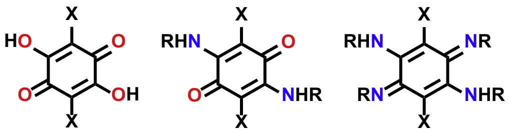

Scheme 1. Benzoquinoid bridging ligands with oxygen and/or nitrogen donor atoms.

2,5-diamino-substituted benzoquinoids have been shown to readily hydrolyze in aqueous reactions with metal ions to instead give 2,5-dihydroxybenzoquinoid metal compounds [10b,14]. Herein, we report the synthesis and crystal structure of a zinc(II) 2,5-diamino-benzoquinonoid chain compound, which, to our knowledge, represents the first example of a structurally-characterized extended solid that contains amino-substituted benzoquinoid bridging ligands.

2. Synthesis and characterization

2.1. General considerations

The ligand 2,5-diamino-3,6-dibromo-1,4-benzoquinone ($^{Br}LH_2$) was prepared following a literature procedure [15]. The solvent *N*,*N*-dimethylformamide (DMF) was dried using a commercial solvent purification system from Pure Process Technology. All other reagents and solvents were obtained from commercial sources without further purification.

2.2. Synthesis of Zn(^{Br}L)(DMF) (**1**)

Solid $^{Br}LH_2$ (151 mg, 0.510 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (294 mg, 0.988 mmol) were dissolved in anhydrous DMF (10 mL) in a 22.5 mL screw-cap borosilicate vial (Qorpak, GLC-01006). The vial was capped and allowed to stand in an isothermal oven at 130 °C for 17 h, during which a dark crystalline solid formed. The vial and its contents were then allowed to cool to ambient temperature, and the mother liquor was decanted. Fresh anhydrous DMF (3 mL) was added to the residual solid and then decanted. This washing process was repeated 10 times, until the supernatant appeared colorless to the eye. The residual solid was washed with diethyl ether five times (3 mL each), and then was collected by filtration. The residue was allowed to dry in air to afford **1** (136 mg, 61%) as a black crystalline solid. Anal. Calcd for $C_9H_9Br_2N_3O_3Zn$ (**1**): C, 25.00; H, 2.10; N, 9.72%. Found: C, 25.36; H, 2.26; N, 9.72%.

2.3. X-ray crystallography

A single crystal of **1** was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The crystallographic data were collected at 100 K on a Bruker APEX II diffractometer equipped with Cu Kα microsource. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker Apex2 v. 2009.1 [16]. The space group was determined using XPREP based on systematic absence and E-statistics [17]. The structure was solved using direct methods under SHELXT and refined with SHELXL using an Olex 2 graphical interface [18]. All zinc, bromine, oxygen, nitrogen, and carbon atoms were located in the electron density difference maps and refined anisotropically. Some restraints of distance and atomic displacement parameters were applied to the coordinated DMF molecule. Ideal positions for hydrogen atoms were calculated and refined as riding models. After the initial refinement, a significant residual electron density was found at 1.3 Å away from bromine atom and normal to the ligand plane, indicating slight rotational disorder of the ligand through the Zn-Zn axis. The disordered portion of the ligand was modeled using a SAME command, and the atomic displacement parameters were constrained to be the same as the main portion of the ligand. The occupancies of the two conformations were refined freely, but sum of occupancies was set to one. This treatment significantly improved the refinement statistics. A summary of crystallographic data is given in Table 1.

2.4. Powder X-ray diffraction

Powder X-ray diffraction data were collected for a polycrystalline sample of **1** in a boron-rich capillary tube with 0.7 mm outer diameter. Data were collected on a Rigaku ATXG diffractometer equipped with Cu Kα radiation, with a tube voltage and current of 50 kV and 240 mA, respectively.

2.5. ^{13}C NMR spectroscopy

The ^{13}C NMR spectra were collected at ambient temperature on a Bruker Avance III 500 MHz instrument equipped with a DCH CryoProbe. The spectrum of $^{Br}LH_2$ was obtained from a solution in DMSO-d_6. Digestion of **1** was carried out by adding a solution of DCl in D_2O (35% w/w, 10 μL) to a suspension of **1** (8.6 mg) in DMSO-d_6 (600 μL). Data were collected following complete dissolution of **1** (ca. 30 min). The chemical shifts of both spectra were corrected using DMSO protons as the internal standard.

2.6. Other physical measurements

Infrared spectra were recorded on a Bruker Alpha FTIR spectrometer equipped with an attenuated total reflectance (ATR) accessory. X-ray photoelectron spectroscopy (XPS) data were carried out on a Thermo Scientific ESCALAB 580Xi instrument equipped with an electron flood gun and a scanning ion gun. Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN). Two-point dc conductivity data were collected at 295 K using a home-built pressed pellet system and a CH Instruments CHI660E electrochemical workstation.

Table 1
Crystallographic data for **1**.

	1
Empirical formula	$C_9H_9Br_2N_3O_3Zn$
Formula weight, g/mol	432.38
Crystal system	Orthorhombic
Space group	*Pnma*
Wavelength, Å	1.54178
Temperature, K	100
a, Å	9.6500(5)
b, Å	14.7981(6)
c, Å	8.8332(7)
α, °	90
β, °	90
γ, °	90
V, Å^3	1261.4(1)
Z	4
ρ_{calcd}, mg/m^3	2.277
μ, mm^{-1}	10.191
Refections coll./unique	7122/1167
R_{int}	0.0505
[a]R_1 ($I > 2\sigma(I)$)	0.0995
[b]wR_2 (all)	0.2333
GoF	1.149

[a] $R_1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$.
[b] $wR_2 = [\Sigma w(F_O^2 - F_C^2)^2/\Sigma w(F_O^2)^2]^{1/2}$.

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