

## Synthesis and Structure of Asymmetric Bis(sulfonamide) Based Copper(II) Complexes: Influence of Diastereomeric Interactions in the Solid State<sup>†</sup>

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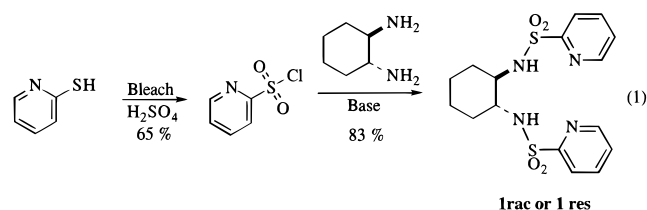
Metalloporphyrins have been the focus of a substantial amount of attention,<sup>1–4</sup> primarily due to their importance in biological systems. Porphyrins have also proven to be extremely useful and efficient in catalytic atom transfer reactions.<sup>5</sup> Many elegant and intricate chiral metalloporphyrin catalysts exhibit impressive reactivity and selectivity.<sup>6–13</sup> Despite these attributes, however, widespread use of metalloporphyrin-based asymmetric catalysts has been hampered by the challenging syntheses of the ligands.

Several groups have sought to mimic the catalytic ability of metalloporphyrins by designing related ligands which are easier

to synthesize.<sup>14–19</sup> In our approach, we have conserved the nitrogen-based tetradentate nature of the porphyrin ligand as well as the dianionic charge, making the ligands isoelectronic.<sup>20</sup>

We have focused on the use of sulfonamide-based ligands<sup>20–25</sup> due to the robust nature of this linkage.<sup>26</sup> Because of the electron-withdrawing ability of the sulfonyl group, the N–H of the sulfonamide has a pK<sub>a</sub> of 10.<sup>27</sup> For this reason, the deprotonated sulfonamide, the sulfonamido group, is only weakly electron donating. We<sup>21,24,28</sup> and others<sup>29–31</sup> have described the enhanced Lewis acidity of bis(sulfonamido) compounds which can coordinate the weakly basic sulfonyl oxygens of the ligand intramolecularly<sup>21,24,29</sup> or intermolecularly, forming dimers.<sup>30,31</sup>

An important feature of our tetradentate ligands is the ability to incorporate asymmetry in close proximity to the metal-binding site (eq 1). The ligand is easily prepared on multigram scale in two steps (eq 1).<sup>20</sup> We have prepared racemic ligand (denoted **1rac**) and resolved ligand with the configuration *R,R* (denoted **1res**).



**1rac** or **1res**

The choice of metal for this study was based on coordination numbers and geometries. Copper(II) was chosen because it forms complexes with square planar geometries but has the propensity to weakly coordinate one or two additional ligands.<sup>32</sup> This latter characteristic can permit association of the individual metal–ligand units.

Coordination of **1rac** to copper(II) was accomplished by combining an acetonitrile solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O with **1rac** and triethylamine (eq 2). Dark blue crystals of **2rac** formed on cooling the solution to 10 °C in 70% yield. Recrystallization from dichloromethane provided crystals suitable for an X-ray structure determination. The structure is the heterochiral dimer

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<sup>†</sup> Dedicated to the memory of Professor Clay M. Sharts.

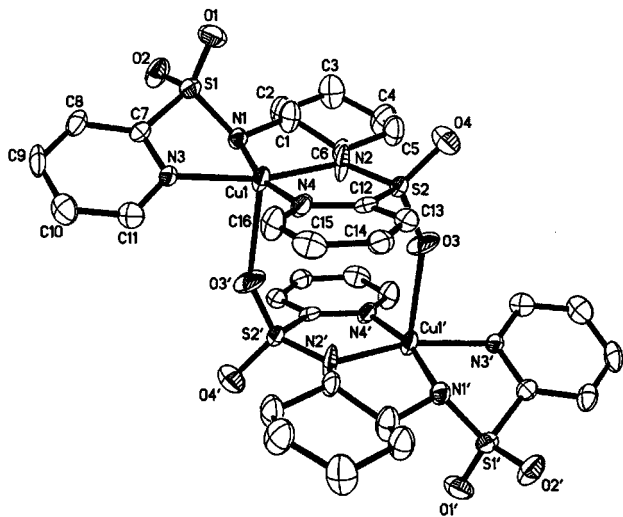
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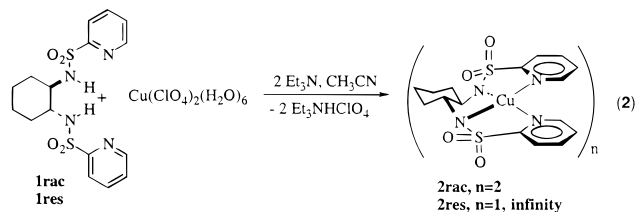
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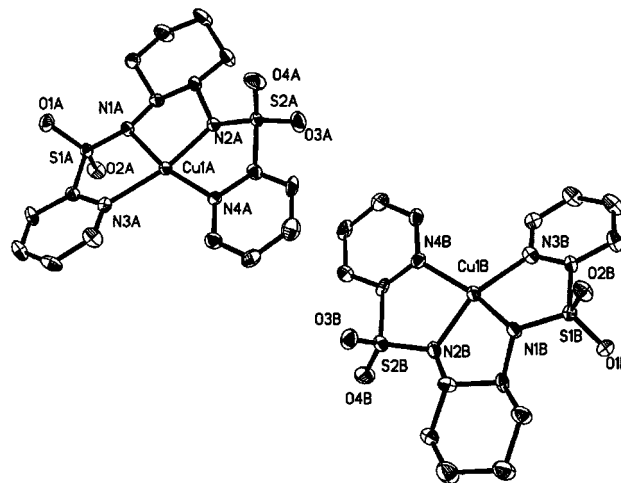
**Figure 1.** Structure of dimeric **2rac**. Important distances (Å) and angles (deg): Cu(1)–N(1) = 1.985(6), Cu(1)–N(2) = 1.951(6), Cu(1)–N(3) = 2.026(6), Cu(1)–N(4) = 2.043(6), Cu(1)–O(3') = 2.328(6), S(1)–O(1) = 1.444(6), S(1)–O(2) = 1.436(6), S(2)–O(3) = 1.451(6), S(2)–O(4) = 1.428(6), N(1)–Cu(1)–N(2) = 83.7(3), N(2)–Cu(1)–N(3) = 165.7(3), N(3)–Cu(1)–N(4) = 103.2(2), N(1)–Cu(1)–N(4) = 165.9(2).

consisting of the *R,R* and *S,S* configurations of **1rac** (Figure

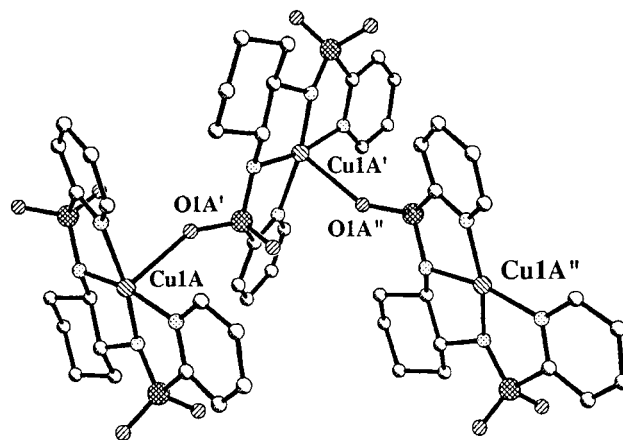


1). Each Cu is a square-based pyramid with the fifth coordination site filled by a sulfonyl oxygen of an adjacent ligand. The Cu–N sulfonamido bond distances are Cu(1)–N(1) 1.985(6) Å and Cu(1)–N(2) 1.951(6) Å, while the Cu–N pyridyl distances are slightly longer with Cu(1)–N(3) 2.026(6) Å and Cu(1)–N(4) 2.043(6) Å. These distances are similar to those in related systems.<sup>33–35</sup> The apical Cu(1')–O(3) sulfonyl distance is longer at 2.328(6) Å, but within bonding distance.<sup>36–38</sup> The bridging sulfonyl S(2)–O(3) distance [1.451(5) Å] is slightly longer than the other S–O distances due to the interaction with Cu(1'). The four nitrogens of the ligand lie nearly in a plane (maximum deviation 0.02 Å). Cu(1) is displaced from this plane toward the sulfonyl oxygen O(3') by 0.18 Å.

The preferential formation of the meso heterochiral dimer in the solid state structure of **2rac** suggests that it may be more stable than the diastereomeric homochiral dimer. In a catalytic system where catalysis takes place at a monomeric metal complex but the resting states of the catalyst are the heterochiral and homochiral dimers, the energy difference between the



**Figure 2.** Structure of **2res**. Important distances (Å) and angles (deg): Cu(1A)–N(1A) = 1.971(8), Cu(1A)–N(2A) = 1.966(7), Cu(1A)–N(3A) = 2.080(8), Cu(1A)–N(4A) = 2.022(8), Cu(1A)–O(1A') = 2.410(8), Cu(1B)–N(1B) = 1.960(8), Cu(1B)–N(2B) = 1.947(7), Cu(1B)–N(3B) = 2.022(6), Cu(1B)–N(4B) = 2.033(9), N(1A)–Cu(1A)–N(2A) = 83.5(3), N(2A)–Cu(1A)–N(3A) = 167.4(3), N(3A)–Cu(1A)–N(4A) = 107.7(3), N(1A)–Cu(1A)–N(4A) = 167.7(3), N(1A)–Cu(1A)–N(3A) = 84.1(3), N(2A)–Cu(1A)–N(4A) = 85.5(3), N(1B)–Cu(1B)–N(2B) = 83.5(3), N(2B)–Cu(1B)–N(3B) = 156.3(3), N(3B)–Cu(1B)–N(4B) = 106.7(3), N(1B)–Cu(1B)–N(4B) = 160.8(3), N(1B)–Cu(1B)–N(3B) = 88.3(3), N(2B)–Cu(1B)–N(4B) = 86.8(3).



**Figure 3.** Polymeric structure of **2res** molecule A. Cu(1A)–O(1A') = 2.410(8).

resting states can have a large effect on the enantioselectivity of the final product.<sup>39–41</sup>

To explore this issue, we prepared the resolved analogue **2res** (eq 2). An ORTEP diagram of **2res** is illustrated in Figure 2. There are two molecules in the asymmetric unit cell. However, the distance from copper to the nearest sulfonyl oxygen in the adjacent molecule in the unit cell is not within bonding distance [Cu(1A)···O(3B) 3.201 Å, Cu(1B)···O(3A) 3.097 Å]. Instead, the Cu(1A) center interacts with the sulfonyl oxygen of a Cu in an equivalent position in a neighboring unit cell to make a polymeric chain [Cu(1A)–O(1A') 2.410(8) Å] (Figure 3). In contrast, the other copper complex in the unit cell is monomeric [Cu(1B)···O(1B') 2.708(9) Å]. In **2res**, the Cu–N sulfonamido

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distances are comparable to the distances found in **2rac** (Figure 1). The geometry about Cu(1A) in the polymer of **2res** is similar to that of Cu(1) in dimer **2rac**. The four nitrogens form a plane with the maximum deviation being 0.026 Å. Cu(1A) is displaced from this plane by 0.075 Å toward the sulfonyl oxygen O(1A'). In contrast, the geometry about Cu(1B), in the monomer of **2res**, is significantly different from either the dimer **2rac** or the polymer of **2res**. There is a notable distortion toward a tetrahedral geometry. The angle between the planes defined by N(1B)–Cu(1B)–N(2B) and N(3B)–Cu(1B)–N(4B) is 28.4°. The interesting differences in the solid state structures which give rise to a dimer (**2rac**) and a polymer and monomer (**2res**) can be attributed to the differences in energies of the hetero- and homochiral dimers in combination with crystal packing forces.

From the solid state characteristics of **2rac** and **2res**, it was anticipated that the homochiral dimer (**2rac**) with two bridging interactions would exhibit a higher degree of association in solution. The cyclic voltammograms of **2res** and **2rac** showed identical behavior in acetonitrile solvent. The voltammetry at a glassy carbon electrode showed the presence of an irreversible oxidation wave at +1.18 V vs SCE and a reduction peak at –0.51 V vs SCE. The oxidation process at +1.18 V can be attributed to formation of a Cu(III) species. The formation of a Cu(II) cation radical species involving ligand oxidation cannot be excluded; however, the voltammogram of the ligand **1rac** did not show any electroactivity in the potential region (–1.0 V to +1.5 V) studied.

The reversibility of the reduction process (Cu<sup>II</sup>/Cu<sup>I</sup>) at –0.51 V is sensitive to the presence of air (oxygen) and potential scan rates, thus indicating the reactive nature of the Cu<sup>I</sup> species. Square planar anionic ligands generally stabilize Cu<sup>II</sup> over Cu<sup>I</sup>, rendering the reduction potential more negative and making the Cu<sup>I</sup> state reactive.

The bonding differences observed in the solid state structures of **2res** and **2rac** are not evident in the voltammetric scans. The disruption of the bridging sulfonyl linkages upon dissolution to form monomeric units may explain this observation. Additionally, the UV–visible spectra showed identical absorption profiles with a d–d absorption band maximum at 596 nm in acetonitrile or methylene chloride solvent.

In summary, we have developed a new class of porphyrin ligand mimics which readily bind copper(II), giving unique copper–sulfonyl oxygen bridging motifs in the solid state. The stability of copper(II) in the square planar geometry results in a weakening of the bridging interactions and disfavors association in solution at room temperature. However, if the strength of this interaction could be increased, through ligand modification or by employing a more Lewis acidic metal, catalysts composed of the bis(sulfonamide) bis(pyridyl) ligands **1rac** and **1res** could exhibit asymmetric amplification. We are currently pursuing research in this area.

## Experimental Section

**General. Cautionary Note:** Although no problems were encountered in this work, care should be used in the handling perchlorate salts.

All reactions were performed under air. Acetonitrile was distilled from calcium hydride. UV–vis spectra were recorded on a HP-8452A diode array spectrometer. All reagents were purchased from Aldrich Chemical Co. and used without further purification. The ligands **1rac** and **1res** were prepared as outlined in our original report.<sup>20</sup>

**Electrochemical Procedures.** All voltammetric experiments were performed using a glassy carbon working electrode, Ag wire as a reference electrode, and a Pt wire as the counter electrode. Tetra-

**Table 1.** Crystal Data and Structure Refinement Parameters for **1** and **2**

	<b>2rac</b>	<b>2res</b>
empirical formula	C <sub>34</sub> H <sub>40</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>4</sub> S <sub>4</sub>	C <sub>18</sub> H <sub>18</sub> CuN <sub>5</sub> O <sub>4</sub> S <sub>2</sub>
fw	1085.9	496.03
<i>a</i> (Å)	8.8047(10)	12.3864(8)
<i>b</i> (Å)	14.221(3)	9.7426(13)
<i>c</i> (Å)	17.101(2)	17.2440(12)
α (deg)	90	90
β (deg)	99.592(8)	99.332(6)
γ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	2111.3(5)	2053(3)
<i>Z</i>	2	4
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>
<i>T</i> (K)	158	293
radiation, λ (Å)	Mo Kα, 0.710 373	Mo Kα, 0.710 373
ρ(calcd) (g/cm <sup>3</sup> )	1.708	1.605
μ (mm <sup>−1</sup> )	1.519	1.303
final <i>R</i> indices <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0556 <i>wR</i> 2 = 0.1285	<i>R</i> 1 = 0.0530 <i>wR</i> 2 = 0.1296
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0925 <i>wR</i> 2 = 0.1517	<i>R</i> 1 = 0.1009 <i>wR</i> 2 = 0.1636

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

tylammonium hexafluorophosphate was used as the supporting electrolyte. All solutions were degassed with nitrogen gas to remove traces of oxygen prior to measurements. The *E*<sup>o</sup> for the ferrocene/ferrocenium redox couple measured using the above electrode system was +0.64 V. This value was used to convert to the SCE reference scale.

**X-ray Crystallographic Procedures.** Crystals were isolated from the mother liquor and immediately immersed in paratone. A crystal was selected for the X-ray diffraction study, mounted in paratone on a quartz fiber, and rapidly placed in a nitrogen gas cold stream of the cryostat of the Siemens diffractometer (or mounted at room temperature in epoxy for **2res**). The crystal was indexed and data collected. Corrections for the effects of absorption anisotropy were done. Structure solutions were performed by direct methods, and structure refinement was done with the programs SHELXS and SHELXL.<sup>42</sup> Crystallographic parameters are given in Table 1, and selected bond distances and angles are provided in the figure captions.

**Synthesis and Characterization of Racemic Copper Dimer 2rac. Synthesis and Characterization of 2rac.** Copper(II) perchlorate, [Cu(ClO<sub>4</sub>)<sub>2</sub>]·6H<sub>2</sub>O (0.100 g, 0.25 mmol), and **1rac** (0.0924 g, 0.25 mmol, 1 equiv) were combined in 5 mL of dry acetonitrile and mixed until approximately 90% of the solids had dissolved, giving a dark green solution. To this solution was slowly added triethylamine (0.070 mL, 0.50 mmol, 2 equiv). The remaining solids dissolved, and the solution became dark blue. The reaction mixture was allowed to stand for 12 h at 10 °C, during which time a fine white precipitate formed. The precipitate was filtered and the solution cooled to 10 °C. Bright blue crystals of **2rac** formed and were isolated by decanting the solvent (81 mg, 0.18 mmol, 71%). Data for **2rac**: mp 216 °C (dec.); no signals were observed by NMR; IR (KBr) 585 (m), 628 (w), 673 (s), 750.0 (w), 773 (m), 809 (m), 895 (m), 974 (m), 1026 (w), 1085 (vs), 1116 (vs), 1148 (vs), 1203 (sh), 1234 (s), 1276 (s), 1366 (w), 1433 (m), 1456 (sh), 1597 (w), 1637 (w, br), 1686 (w), 2850 (w), 2922 (m) cm<sup>−1</sup>; UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) λ = 300 nm (ε = 2470), 370 nm (ε = 1370), 696 nm (ε = 240).

Crystals of **2rac** suitable for an X-ray structure determination study were grown by dissolving **2rac** in CH<sub>2</sub>Cl<sub>2</sub> followed by vapor diffusion of ether into the solution at 10 °C.

**Synthesis and Characterization of Resolved Copper Complex 2res.** Copper(II) perchlorate, [Cu(ClO<sub>4</sub>)<sub>2</sub>]·6H<sub>2</sub>O (0.100 g, 0.25 mmol), and ligand **1rac** (0.0924 g, 0.25 mmol, 1 equiv) were combined in 5 mL of acetonitrile and mixed until the majority of the ligand had dissolved, giving a dark green solution. To this solution was slowly

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added triethylamine (0.070 mL, 0.50 mmol, 2 equiv) by syringe. On addition of the amine, the remaining solids dissolved and the solution became dark blue. The reaction mixture was allowed to stand for 12 h at 10 °C, during which time a fine white precipitate had formed. The precipitate was filtered through a glass filter frit. The volume of the solvent was reduced to 2 mL and the solution collected and cooled to 10 °C. On standing, crystals of **2res** formed as bright blue needles and were isolated by decanting the solvent, to yield 106 mg (0.21 mmol, 85.3%). Data for **2res**: mp 210 °C (dec.); IR (KBr) 584 (m), 619 (w), 661 (w), 746 (m), 777 (m), 811 (m), 898 (m), 970 (m), 1026 (w), 1089 (vs), 1118 (vs), 1152 (vs), 1207 (s), 1234 (s), 1269 (s), 1361 (w), 1437 (m), 1456 (sh), 1596 (m), 1633 (w), 1689 (m), 2859 (w), 2938 (w)  $\text{cm}^{-1}$ ; no signals were observed by NMR. Anal. Calcd for  $\text{C}_{18}\text{H}_{21}\text{N}_5\text{O}_4\text{S}_2\text{Cu}$ : C, 43.32; H, 4.24; N, 14.03. Found: C, 43.41; H, 4.11; N, 13.91.

Crystals of **2res** suitable for an X-ray structure determination study were grown by dissolving **2res** in acetonitrile followed by vapor diffusion of ether into the solution at 10 °C.

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**Supporting Information Available:** The X-ray crystal structure data for **2rac** and **2res** including a diagram of the polymer of **2res**. For the X-ray structures, tables of final atomic coordinates for the non-hydrogen atoms, anisotropic thermal parameters, a complete list of bond distances and angles, and complete crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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