

# Copper(II) Complexes of Schiff-Base and Reduced Schiff-Base Ligands: Influence of Weakly Coordinating Sulfonate Groups on the Structure and Oxidation of 3,5-DTBC

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**Keywords:** Biomimetic studies / Copper / Schiff-base complexes / Organosulfonate ligands / Catecholase activity / Magnetic properties

The copper(II) complexes of the Schiff-base ligands H<sub>2</sub>Sams and H<sub>2</sub>Saes and the reduced Schiff-base ligands H<sub>2</sub>Sam and H<sub>2</sub>Sae formed between salicylaldehyde and aminomethanesulfonic acid or 2-aminoethanesulfonic acid (taurine) have been synthesized in moderate yields. The solid-state structures of the five dinuclear complexes, [Cu<sub>2</sub>(Sams)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**), [Cu<sub>2</sub>(Sam)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (**2**), [Cu<sub>2</sub>(Saes)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**3**), [Cu<sub>2</sub>(Sae)<sub>2</sub>]·2H<sub>2</sub>O (**4**), and [Cu<sub>2</sub>(Sae)<sub>2</sub>(DMF)<sub>2</sub>]·2DMF (**5**), have been determined by X-ray crystallography, showing that the Cu<sup>II</sup> centers have distorted square-pyramidal geometry. The Schiff-base copper complexes **1** and **3** have hydrogen-bonded 2D sheet structures while the reduced Schiff-base complexes **4** and **5** display a 2D coordination network and a

hydrogen-bonded 2D structure respectively. All these complexes have been investigated for their catecholase activity and activity measurements have been compared with those of dinuclear copper(II) complexes of similar ligands obtained with carboxylate analogues of the corresponding sulfonic acids; these studies show that **4** has significantly higher activity. Further, a strong antiferromagnetic interaction between Cu<sup>II</sup> ions in dimeric complexes **1** [ $J = -9.04(2) \text{ cm}^{-1}$ ], **3** [ $J = -272(4) \text{ cm}^{-1}$ ], and **4** [ $J = -237(4) \text{ cm}^{-1}$ ] has been observed.

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## Introduction

In the past decades, significant progress has been made in understanding the coordination chemistry of copper(II) complexes of various Schiff-base ligands.<sup>[1]</sup> Most of the model studies of the metal complexes of Schiff-base ligands containing salicylaldehyde and amino acids have focused upon the binding mode of these ligands.<sup>[2]</sup> X-ray crystal structures of complexes thus obtained demonstrated that the Schiff-base ligand acts as a tridentate moiety, coordinating through the phenolato oxygen, imine nitrogen, and carboxylate oxygen.

Our research group is interested in tridentate reduced Schiff-base ligands, specifically *N*-(2-hydroxybenzyl)amino acids, as they are more flexible because of the reduction of the C=N bond of the Schiff base, and help to overcome the ligand instability. Further, in addition to their potential

hydrogen-bond donor-acceptor functionalities, these ligands can form conformationally flexible five- and six-membered rings upon complexation. Several copper complexes of reduced Schiff-base ligands formed between salicylaldehyde and amino acids were explored to serve as models for the intermediate species in biological racemization and transamination reactions.<sup>[3]</sup> Making use of these advantages, we employed such reduced Schiff-base ligands to synthesize dinuclear Cu<sup>II</sup> and Zn<sup>II</sup> complexes that exhibit interesting structural transformations in the solid state.<sup>[4]</sup> Further, in our recent report, we showed that incorporation of an additional carboxylate group in the side arm of the ligand *N*-(2-hydroxybenzyl)-L-glutamic acid formed between salicylaldehyde and L-glutamic acid resulted in a novel structural display of a spiral staircase conformation.<sup>[5]</sup> Copper(II) complexes of the reduced Schiff-base ligand derived from salicylaldehyde and histidine have been found to self-assemble to form a capsule incorporating four pyridine molecules.<sup>[6]</sup>

Various dicopper active sites found in copper-containing metalloenzymes have similar structural aspects with three histidine donors for each of the two Cu centers, which are separated by a distance of about 3.5 Å, and catechol oxidase as one of the prominent members of the type III copper proteins that catalyze the two-electron oxidation of *ortho*-diphenols to the corresponding quinones.<sup>[7]</sup> Conse-

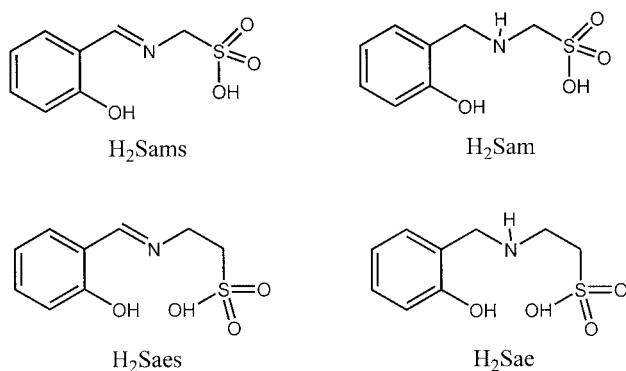
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quently, quite a number of dinuclear copper complexes have been investigated as biomimetic catalysts for catechol oxidation by employing the most common and convenient model substrate, 3,5-di-*tert*-butylcatechol (3,5-DTBC), which can be oxidized to 3,5-di-*tert*-butylquinone (3,5-DTBQ).<sup>[8]</sup> With regard to this, we have recently reported a series of dinuclear copper(II) complexes of the tridentate and binucleating reduced Schiff-base ligands and their functional relationship with catecholase activity.<sup>[9]</sup> Apart from the reduced Schiff-base ligands with carboxylate donor group, their sulfonic acid analogues are expected not only to improve solubility in aqueous media but also form interesting supramolecular architectures by modifying the connectivity at the metal centers as well as the hydrogen-bonding pattern.<sup>[10]</sup> However, the coordination chemistry of transition metals with a similar ligand system containing organosulfonate species is not well documented.<sup>[11]</sup> Despite the available literature showing the organosulfonate anions as good hydrogen-bonding acceptors to form strongly hydrogen-bonded networks,<sup>[12]</sup> there are few metal-based supramolecular arrays in the literature.<sup>[13]</sup>

Encouraged by our previous results, we were prompted to synthesize such tridentate *N*-(2-hydroxybenzyl)aminoethane/ethanesulfonic acids (Scheme 1), and their corresponding dinuclear copper(II) complexes of both Schiff-base and reduced Schiff-base ligands. In order to evaluate these complexes for the effect of the sulfonate donor group, compared to the corresponding carboxylate analogues, on the crystal structures and the consequent influence on the catecholase activity, herein we report and highlight different structural features between Schiff-base and reduced Schiff-base dicopper(II) complexes, and their catecholase activity. Variable temperature magnetic studies have also been discussed for the Cu<sup>II</sup> complexes containing *syn-syn* O–S–O-bridged **1** and **3** and phenoxo-bridged **4**, which can mediate magnetic interaction effectively within the dimeric Cu unit.



Scheme 1. Ligands employed for complexation.

## Results and Discussion

Copper complexes **1** and **3** were prepared by treating copper(II) nitrate trihydrate solution with the Schiff bases formed in situ between salicylaldehyde and aminomethanesulfonic acid and/or aminoethanesulfonic acid. The re-

duced Schiff-base complex [Cu<sub>2</sub>(Sam)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O (**2**) was obtained by treating a copper(II) nitrate trihydrate solution with H<sub>2</sub>Sam generated in situ. On the other hand, reduced Schiff-base H<sub>2</sub>Sae was synthesized first and then complexed with copper(II) acetate monohydrate to obtain [Cu<sub>2</sub>(Sae)<sub>2</sub>]·2H<sub>2</sub>O (**4**). The complex [Cu<sub>2</sub>(Sae)<sub>2</sub>(DMF)<sub>2</sub>]·2DMF (**5**) resulted when **4** was recrystallized from the DMF/acetone solvent mixture. We were unable to isolate *N*-(2-hydroxybenzyl)aminopropanesulfonic acid or prepare its Cu<sup>II</sup> complex in situ as in the case of the H<sub>2</sub>Sam ligand. Complexes **1–4** show absorption bands at 3400, 3443, and 3410 cm<sup>−1</sup> corresponding to the presence of water molecules. The C=N stretching frequencies are observed at 1629 cm<sup>−1</sup> in **1** and 1617 cm<sup>−1</sup> in **3**. As the C=N bond is reduced in **2**, **4**, and **5**, the N–H stretching frequencies appeared in the range of 2920–2935 cm<sup>−1</sup>. The frequencies characteristic of the S–O stretching modes are observed in the range 1000–1380 cm<sup>−1</sup>.<sup>[14]</sup>

The electronic spectra of **1** and **3** in water display weak bands at 678 and 688 nm followed by intense bands at 367 and 322 nm respectively. The high intensity can be attributed to the delocalization of charge in the conjugated Schiff base. Copper(II) complexes of Schiff bases and related ligands exhibit weak bands in the range 620–680 nm which are due to d–d transitions.<sup>[15]</sup> For an octahedral geometry, the expected <sup>2</sup>E<sub>g</sub> to <sup>2</sup>T<sub>2g</sub> transition takes place at around 800 nm. This band will undergo a significant blue shift when octahedral geometry distorts to square pyramidal and square planar structure.<sup>[16]</sup> For the reduced Schiff-base copper(II) complexes with square pyramidal geometry, the d–d transitions and charge transfer transitions generally occur in the ranges 650–720 and 360–450 nm respectively.<sup>[9,17]</sup> In the case of **2**, **4**, and **5** the absorption bands at 717–736 nm correspond to d–d transitions and a strong band at 405–420 nm is due to ligand-to-metal charge transfer.

TG analysis of **1** showed a weight loss of 6.8% (calculated 6.1%) for the loss of two aqua ligands in the temperature range 159–192 °C. In **2**, the loss of three water molecules, including two aqua ligands and a lattice water, was indicated by a weight loss of 8.1% (calculated 8.4%) in the temperature range 148–183 °C. Similarly, a weight loss of 11.7% (calculated 11.0%) corresponding to two aqua ligands and two lattice water molecules has been found to occur at 30–155 °C in **3**. TG weight loss of 5.7% (calculated 5.8%) agrees well with the loss of two lattice water molecules in **4**.

## Description of X-ray Crystal Structures

Selected crystallographic data and refinement details are displayed in Table 1.

### Crystal Structure of [Cu<sub>2</sub>(Sams)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**)

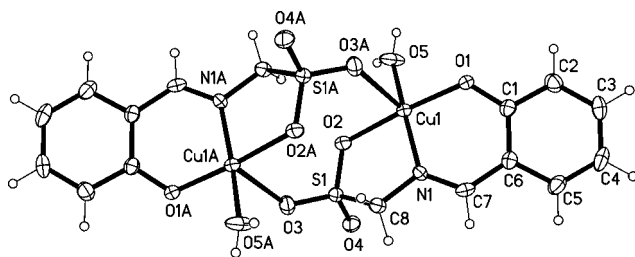
Dark green prismatic single crystals of **1** suitable for single-crystal X-ray crystallographic studies were obtained from the filtrate of the reaction mixture on slow evaporation. Compound **1** is a centrosymmetric dimer with copper centers assuming square pyramidal geometry ( $\tau = 0.16$ ).<sup>[18]</sup>

Table 1. Crystallographic data and structure refinement details for **1**, **3**, **4**, and **5**.

Complex	<b>1</b>	<b>3</b>	<b>4</b>	<b>5</b>
Formula	C <sub>16</sub> H <sub>18</sub> Cu <sub>2</sub> N <sub>2</sub> O <sub>10</sub> S <sub>2</sub>	C <sub>9</sub> H <sub>13</sub> CuNO <sub>6</sub> S	C <sub>18</sub> H <sub>23</sub> Cu <sub>2</sub> N <sub>2</sub> O <sub>9</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>46</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>12</sub> S <sub>2</sub>
Formula mass	589.52	326.8	602.6	873.93
<i>T</i> [K]	223(2)	223(2)	223(2)	223(2)
Wavelength, $\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> [Å]	7.0092(7)	6.9079(7)	10.8222(7)	13.2137(9)
<i>b</i> [Å]	9.0004(8)	9.226(1)	8.7872(6)	9.7141(7)
<i>c</i> [Å]	9.0516(8)	10.439(1)	11.9314(8)	14.944(1)
$\alpha$ [°]	97.012(2)	109.042(2)	90	90
$\beta$ [°]	109.829(2)	101.162(2)	108.024(1)	99.130(1)
$\gamma$ [°]	107.720(2)	104.906(2)	90	90
<i>V</i> [Å <sup>3</sup> ]	495.24(8)	579.0(1)	1079.0(1)	1893.9(2)
<i>Z</i>	1	1	2	2
<i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.977	1.875	1.855	1.532
$\mu$ [mm <sup>-1</sup> ]	2.420	2.086	2.220	1.299
Reflections collected	2880	4727	6007	14925
Independent reflections	1754	3168	1902	5330
<i>R</i> <sub>int</sub>	0.0233	0.0174	0.0195	0.0238
Gof	1.024	1.034	0.741	1.013
Final <i>R</i> [ <i>I</i> > 2 $\sigma$ ], <i>R</i> <sub>1</sub> <sup>[a]</sup>	0.0346	0.0380	0.0226	0.0399
<i>wR</i> <sub>2</sub> <sup>[b]</sup>	0.0822	0.0848	0.0612	0.1023

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

At each copper center, the basal plane of the square pyramid is occupied by three oxygen atoms, one each from the phenolate group [Cu1–O1, 1.898(2) Å], the sulfonate group [Cu1–O2, 2.019(2) Å], and the aqua ligand [Cu1–O5, 1.932(2) Å]; and nitrogen [Cu1–N1, 1.936(3) Å] from the imine group. The apical sites of the Cu<sup>II</sup> centers have *anti* configuration and are occupied by the oxygen atoms [Cu1–O3A, 2.393(3) Å; Cu1A–O3, 2.393(3) Å] of the sulfonate group from the neighboring molecule as shown in Figure 1. Selected bond lengths and bond angles are given in Table 2.

Figure 1. An ORTEP diagram of **1**.

Unlike the complexes obtained with reduced Schiff bases displaying the phenoxo-bridged dinuclear Cu<sup>II</sup> centers with the usual Cu...Cu distance of about 3 Å, H<sub>2</sub>Sams gave rise to the dinuclear copper core with Cu...Cu separation of 5.12 Å without bridging phenolate moiety. Instead, the centrosymmetric dinuclear core forms an interesting eight-membered ring consisting of Cu1, O2, S1, O3, Cu1A, O2A, S1A, and O3A (Figure 1). Further, compared with the phenolato-bridged structures formed by the reduced Schiff-base Cu<sup>II</sup> compounds, formation of an entirely different structure of **1** may be attributed to kinetic factors, as several phenolato-bridged dinuclear complexes have been reported in the literature.<sup>[19–21]</sup>

The dimers are packed in the solid state to give a hydrogen-bonded 2D structure in the *ac* plane (Figure 2). Two types of complementary hydrogen bonds are present: the first one is between the phenoxo oxygen and one of the hydrogen atoms of the aqua ligand from the adjacent dimer along the *c*-direction; the next one is between the free oxygen atom of the sulfonate group with another hydrogen atom of the aqua ligand, normal to (100) plane. In addition, these 2D sheets are also supported by C–H...O hydrogen-bonding interactions, C(3)–H(3)...O(4), 2.53 Å; C(7)–H(7)...O(4), 2.52 Å, which are considered medium strong when compared with the shorter and stronger C–H...O interac-

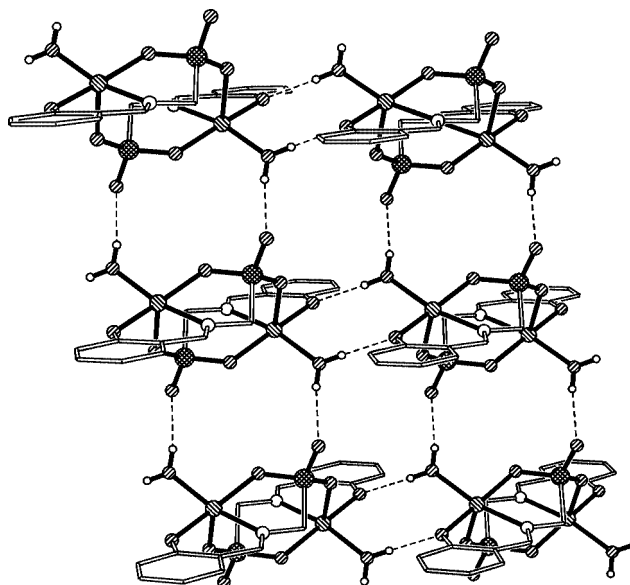
Figure 2. Hydrogen-bonded 2D sheet structure of **1** in *ac* plane.

Table 2. Selected bond lengths [Å] and angles [°] in **1**, **3**, **4**, and **5**.

Compound <b>1</b>			
Cu(1)–O(1)	1.898(2)	S(1)–O(2)–Cu(1)	117.7(1)
Cu(1)–O(5)	1.932(2)	S(1)–O(3)–Cu(1) <sup>[a]</sup>	131.6(1)
Cu(1)–N(1)	1.936(3)	O(1)–Cu(1)–O(5)	91.3(1)
Cu(1)–O(2)	2.019(2)	O(1)–Cu(1)–N(1)	92.2(1)
Cu(1)–O(3) <sup>[a]</sup>	2.393(3)	O(5)–Cu(1)–N(1)	165.8(1)
O(3)–Cu(1) <sup>[a]</sup>	2.393(3)	O(1)–Cu(1)–O(2)	175.2(1)
N(1)–C(7)	1.291(4)	O(1)–Cu(1)–O(3) <sup>[a]</sup>	96.82(1)
N(1)–C(8)	1.452(4)	O(5)–Cu(1)–O(3) <sup>[a]</sup>	89.1(1)
Cu(1)···Cu(1) <sup>[a]</sup>	5.12	N(1)–Cu(1)–O(3) <sup>[a]</sup>	104.2(1)
Compound <b>3</b>			
Cu(1)–O(1)	1.886(2)	S(1)–O(2)–Cu(1)	131.3(1)
Cu(1)–O(2)	1.967(2)	S(1)–O(3)–Cu(1) <sup>[a]</sup>	134.76(1)
Cu(1)–N(1)	1.968(2)	O(1)–Cu(1)–O(2)	168.87(8)
Cu(1)–O(5)	1.989(2)	N(1)–Cu(1)–O(5)	166.92(9)
Cu(1)–O(3) <sup>[a]</sup>	2.410(2)	O(1)–Cu(1)–N(1)	94.08(9)
C(7)–N(1)	1.282(3)	O(2)–Cu(1)–N(1)	97.04(8)
N(1)–C(8)	1.479(3)	O(1)–Cu(1)–O(5)	85.74(9)
O(3)–Cu(1) <sup>[a]</sup>	2.410(2)	O(2)–Cu(1)–O(5)	83.56(8)
Cu(1)···Cu(1) <sup>[a]</sup>	5.33	O(1)–Cu(1)–O(3) <sup>[a]</sup>	87.32(8)
		O(2)–Cu(1)–O(3) <sup>[a]</sup>	89.54(7)
		N(1)–Cu(1)–O(3) <sup>[a]</sup>	103.30(8)
		O(5)–Cu(1)–O(3) <sup>[a]</sup>	89.76(8)
Compound <b>4</b>			
Cu(1)–O(1) <sup>[a]</sup>	1.931(1)	S(1)–O(2)–Cu(1)	120.58(8)
Cu(1)–O(1)	1.972(1)	S(1)–O(4)–Cu(1) <sup>[c]</sup>	132.93(9)
Cu(1)–N(1)	1.986(1)	O(1) <sup>[a]</sup> –Cu(1)–O(1)	78.09(6)
Cu(1)–O(2)	2.002(1)	O(1) <sup>[a]</sup> –Cu(1)–N(1)	172.15(7)
Cu(1)–O(4) <sup>[b]</sup>	2.330(1)	O(1)–Cu(1)–N(1)	94.31(6)
O(1)–Cu(1) <sup>[a]</sup>	1.931(1)	O(1) <sup>[a]</sup> –Cu(1)–O(2)	95.32(6)
O(4)–Cu(1) <sup>[c]</sup>	2.330(1)	O(1)–Cu(1)–O(2)	152.72(7)
Cu(1)–O(1) <sup>[a]</sup>	1.931(1)	O(1) <sup>[a]</sup> –Cu(1)–O(4) <sup>[b]</sup>	94.63(6)
C(7)–N(1)	1.494(3)	O(1)–Cu(1)–O(4) <sup>[b]</sup>	99.55(6)
N(1)–C(8)	1.476(3)	N(1)–Cu(1)–O(4) <sup>[b]</sup>	84.60(6)
O(4)–Cu(1) <sup>[c]</sup>	2.330(1)	O(2)–Cu(1)–O(4) <sup>[b]</sup>	107.40(6)
Cu(1)···Cu(1) <sup>[a]</sup>	3.031(5)	O(2)–Cu(1)–Cu(1) <sup>[a]</sup>	129.59(5)
		O(4) <sup>[b]</sup> –Cu(1)–Cu(1) <sup>[a]</sup>	99.17(4)
Compound <b>5</b>			
Cu(1)–O(1) <sup>[a]</sup>	1.958(1)	O(1) <sup>[a]</sup> –Cu(1)–O(1)	77.96(7)
Cu(1)–O(1)	1.981(1)	O(1) <sup>[a]</sup> –Cu(1)–O(2)	95.31(7)
Cu(1)–N(1)	1.991(1)	O(1) <sup>[a]</sup> –Cu(1)–N(1)	172.38(7)
C(7)–N(1)	1.496(3)	O(1)–Cu(1)–O(2)	156.95(8)
Cu(1)···Cu(1) <sup>[a]</sup>	3.06		

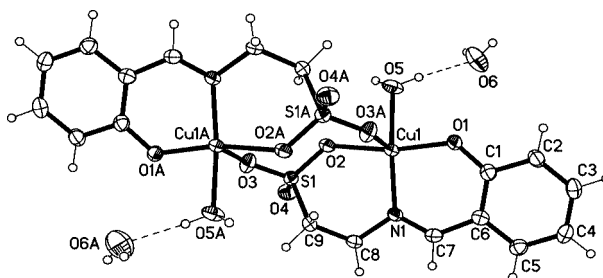
[a] Symmetry transformations used to generate equivalent atoms  $-x + 1, -y, -z$  in **1** and **3**;  $-x + 1, -y + 1, -z + 1$  in **4** and **5**. [b]  $-x + 3/2, y - 1/2, -z + 3/2$ . [c]  $-x + 3/2, y + 1/2, -z + 3/2$ .

tions of about 2.0 Å available in the literature.<sup>[22]</sup> Hydrogen bond parameters in **1** are tabulated in Table 3.

### Crystal Structure of $[\text{Cu}_2(\text{Saes})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**3**)

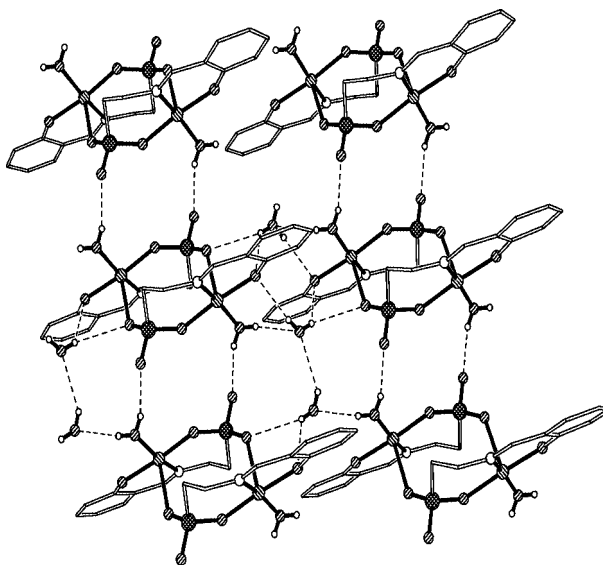
Compound **3** is also a binuclear complex of formula  $[\text{Cu}_2(\text{Saes})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  with a crystallographic center of inversion as in **1**. An ORTEP diagram of **3** with numbering scheme is shown in Figure 3. Selected bond lengths and bond angles are given in Table 2. Each  $\text{Cu}^{\text{II}}$  center has square pyramidal geometry.

The ligand connectivity in **3** is very similar to that found in **1** except that this Saes dianion forms two six-membered rings. The ring expansion is due to an additional methylene group in the  $\text{H}_2\text{Saes}$  ligand, which reduces the ring strain

Figure 3. An ORTEP diagram of **3**.

and thus lowers the  $\tau$ -value to 0.03. As observed in **1**, the dinuclear core in **3** also shows the axial coordination mode by sulfonate oxygen atoms in the centrosymmetric dimer. The introduction of a  $-\text{CH}_2$  group in the  $\text{H}_2\text{Saes}$  ligand changed a five-membered ring to a six-membered ring and hence increased the  $\text{Cu} \cdots \text{S}$  distances (3.01 Å in **1** vs 3.15 Å in **3**). This is also reflected in the widening of the  $\text{Cu(1)–O(2)–S(1)}$  angle from  $117.7^\circ$  in **1** to  $131.3^\circ$  in **3** and an increase in the  $\text{Cu} \cdots \text{Cu}$  separation to 5.33 Å.

Compound **3** also forms hydrogen-bonded sheets similar to **1** (Figure 4). However, a water molecule is strongly hydrogen bonded between the phenoxo oxygen atom and the aqua ligand. The second hydrogen atom of the lattice water is disordered and found to be hydrogen bonded to another lattice water molecule as well as to other oxygen atoms of the sulfonate group. Table 3 shows the hydrogen bond parameters.

Figure 4. Hydrogen-bonded 2D sheets in **3**.

### Crystal Structure of $[\text{Cu}_2(\text{Sae})_2] \cdot 2\text{H}_2\text{O}$ (**4**)

When the  $\text{C}=\text{N}$  double bond is reduced, the complexation behavior of the Sae dianion is completely different from that of the Saes dianion. The Sae ligand with flexible backbone behaves like other reduced Schiff-base ligands in terms of forming a phenolato-bridged  $\text{Cu}^{\text{II}}$  dimer having the expected connectivity of the donor atoms.<sup>[4,9]</sup> A perspective view of **4** exhibiting the coordination environments

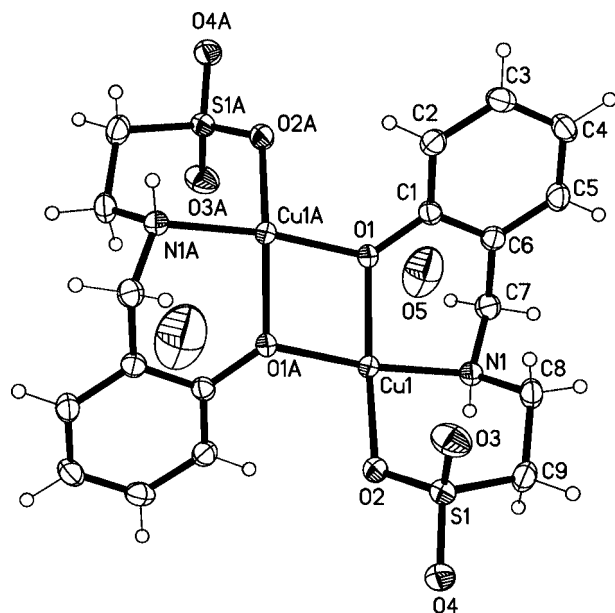


Table 3. Hydrogen bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] in **1**, **3**, **4**, and **5**.

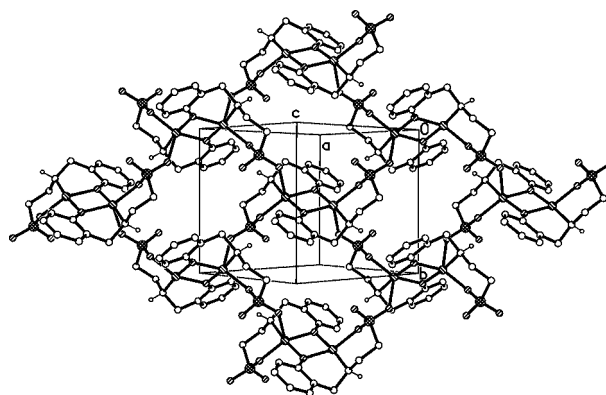
Complex	D–H	$d(\text{D–H})$	$d(\text{H–A})$	$\angle\text{DHA}$	$d(\text{D–A})$	A	Symmetry
<b>1</b>	O5–H5A	0.80(4)	1.98(4)	171(4)	2.775(5)	O4	$-x, -y, -z$
	O5–H5B	0.78(4)	1.85(3)	178(6)	2.626(4)	O1	$1 - x, -y, 1 - z$
<b>3</b>	C3–H3 <sup>[a]</sup>	0.94	2.53	147	3.358(5)	O4	$1 - x, 1 - y, 1 - z$
<b>4</b>	C7–H7 <sup>[a]</sup>	0.94	2.52	172	3.453(4)	O4	$1 - x, 1 - y, -z$
<b>5</b>	O5–H5A	0.81(3)	2.00(3)	156(3)	2.761(3)	O4	$-x, -y, -z$
	O5–H5B	0.81(2)	1.87(2)	166(4)	2.666(4)	O6	$-x, -y, -z$
	O6–H6A	0.81(3)	2.17(3)	157(5)	2.927(7)	O6	$-x, -y, 1 - z$
	O6–H6B	0.81(4)	2.45(4)	140(4)	3.108(4)	O3	$x, y, 1 + z$
	O6–H6B	0.81(4)	2.31(5)	142(4)	2.987(5)	O1	$1 - x, -y, 1 - z$
	N1–H1 <sup>[a]</sup>	0.92	2.32	144	3.144(2)	O2	$3/2 - x, -1/2 + y, 3/2 - z$
	N1–H1	0.92	2.20	145	3.007(3)	O3	$3/2 - x, 1/2 + y, 3/2 - z$
	C9–H9B <sup>[a]</sup>	0.98	2.20	165	3.438(3)	O4	$3/2 - x, 1/2 + y, 3/2 - z$
	C10–H10 <sup>[a]</sup>	0.94	2.54	153	3.406(3)	O4	$1 - x, 1 - y, 1 - z$
	C12–H12A <sup>[a]</sup>	0.97	2.57	156	3.482(4)	O4	$1 - x, 1 - y, 1 - z$

[a] The hydrogen atoms were placed in calculated positions.

around the  $\text{Cu}^{\text{II}}$  atoms is shown in Figure 5. Selected bond lengths and bond angles in **4** are shown in Table 2. The phenolato oxygen atoms, a nitrogen atom from the imine group, and an oxygen atom of the sulfonate group form the basal square. The apical site in each  $\text{Cu}^{\text{II}}$  center is occupied by another oxygen atom of the sulfonate group from the neighboring dimer. This interdimer connectivity leads to the formation of a 2D (4, 4) network structure as shown in Figure 6. The two axial oxygen atoms have *trans* geometry due to the crystallographic center of inversion present at the center of the  $\text{Cu}_2\text{O}_2$  ring. Such geometry has also been observed in several  $\text{Cu}^{\text{II}}$  dimers having nonchiral reduced Schiff-base ligands.<sup>[9]</sup> Interestingly the infinite 2D network structure with (4, 4) net formed in **4** is the first of its kind observed in the  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  complexes containing reduced Schiff-base ligands although these nets are ubiquitous in the literature.<sup>[23]</sup>

Figure 5. An ORTEP diagram of **4**.

The N–H proton is weakly hydrogen bonded to one of the sulfonate oxygen atoms ( $\text{N1–H1}\cdots\text{O2}$ , 2.324  $\text{\AA}$ ). The

Figure 6. A portion of the 2D structure in **4**.

intermolecular  $\text{N–H}\cdots\text{O}$  hydrogen bond between the  $\text{NH}_2$  and sulfonate groups in the solid state and in solution has been utilized as a crystal engineering tool.<sup>[12]</sup> The properties and the functions of the  $\text{N–H}\cdots\text{O}$  hydrogen bonds involving coordinated  $-\text{SO}_3^-$  groups in a dinuclear calcium complex have been reported.<sup>[24]</sup> As in **1**, medium strong  $\text{C–H}\cdots\text{O}$  hydrogen bonds have also been observed in the solid state.

#### Crystal Structure of $[\text{Cu}_2(\text{Sae})_2(\text{DMF})_2]\cdot 2\text{DMF}$ (**5**)

Complex **5** is formed upon recrystallization of **4** from strongly coordinating solvent DMF. The axial sulfonate groups in **4** are replaced by DMF molecules in **5** and hence discrete dinuclear compounds are formed. Two more DMF molecules were found in the crystal lattice. The crystal packing of **5** generated 2D hydrogen-bonded polymeric structures parallel to the  $(10\bar{1})$  planes. The solid-state structure exhibits  $\text{N–H}\cdots\text{O}$  hydrogen bonding between one of the sulfonate oxygen and NH hydrogen atoms (Table 3).

#### Magnetic Properties of **1**, **3**, and **4**

The temperature dependences of  $\chi_m$  and  $\chi_m T$  for crystalline samples of **1**, **3**, and **4** are presented in Figure 7. For compound **1**,  $\chi_m$  increases upon cooling and reaches a maximum at 16 K; the data above 30 K can be well fitted with the Curie–Weiss law [ $\chi_m = C/(T-\theta)$ ], giving  $C =$

$0.802 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ , and  $\theta = -12.7(5) \text{ K}$ . The maximum and negative Weiss constant suggests an antiferromagnetic coupling between  $\text{Cu}^{\text{II}}$  ions. The susceptibility data in the 2–330 K range were fitted with a  $\text{Cu}_2$  dimer model ( $H = -2JS_1S_2$ ), giving the intradimer coupling  $J = -9.04(2) \text{ cm}^{-1}$ , and  $g = 2.002(3)$  with  $R = 2.3 \times 10^{-4}$  ( $R = \Sigma[(\chi_{\text{m}})_{\text{obs}} - (\chi_{\text{m}})_{\text{calc}}]^2 / \Sigma[(\chi_{\text{m}})_{\text{obs}}]^2$ ).

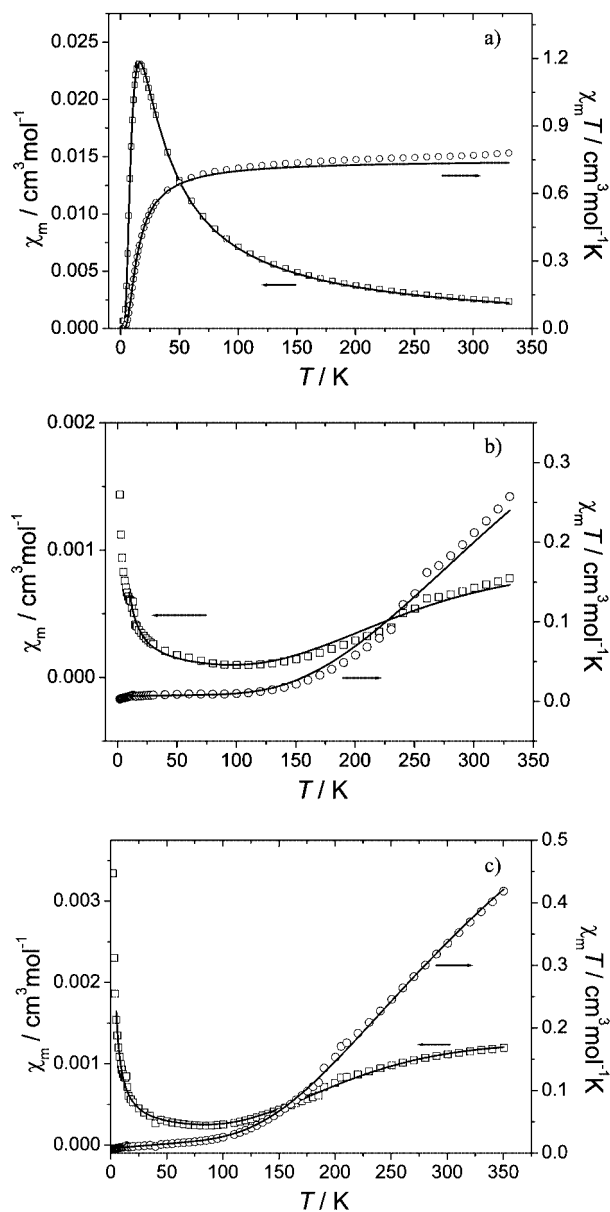


Figure 7. The temperature dependences of  $\chi_{\text{m}}$  and  $\chi_{\text{m}}T$  in the range of 2–350 K for a) **1**, b) **3**, and c) **4**. The solid lines are fits using a  $\text{Cu}_2$  dimer model.

Compounds **3** and **4** show similar behavior; on lowering the temperature,  $\chi_{\text{m}}$  decreases gradually, and there is an increase below about 100 K while the  $\chi_{\text{m}}T$  value even at 330 or 350 K is quite small compared with the expected value of  $0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for two noninteracting  $\text{Cu}^{\text{II}}$  ions. Upon cooling it decreases rapidly to a value close to zero at 2 K. The increase of  $\chi_{\text{m}}$  at low temperature is probably due to

trace paramagnetic impurity ( $\rho$ ). Overall, the data suggest a strong antiferromagnetic coupling between the adjacent  $\text{Cu}^{\text{II}}$  ions in **3** and **4**. Based on the structure of **3**, two  $\text{Cu}^{\text{II}}$  ions are bridged by two sulfonate O–S–O bridges in *syn-syn* mode with  $\text{Cu} \cdots \text{Cu}$  separation at  $5.32 \text{ \AA}$ . Although the distance is quite large compared to the phenoxo-bridged  $\text{Cu}_2$  in **4** with a distance of  $3.03 \text{ \AA}$ , the basal planes of the two  $\text{Cu}^{\text{II}}$  ions are almost parallel, which might favor the overlap of  $d_{x^2-y^2}$  orbitals of  $\text{Cu}^{\text{II}}$  ions within the dimer. On the other hand, the coupling between the dinuclear moiety in the 2D layer of **4** is negligible, as expected, because of both the *anti-syn* sulfonate bridging mode and the orthogonal relationship of the planes of the neighboring  $\text{Cu}_2\text{O}_2$ .<sup>[4d]</sup> Therefore, the magnetic data of **3** and **4** can be analyzed by fitting the susceptibilities to an equation calculated using an  $H = -2JS_1S_2$  Hamiltonian for a dimer plus impurity of monomer model. The parameters have their usual meanings. As shown in Figure 7b and 7c, quite good fits were obtained for **3**:  $J = -272(4) \text{ cm}^{-1}$ ,  $g = 2.05(5)$ ,  $\rho = 0.0164$ ;  $\text{Na} = 22 \times 10^{-6}$  with  $R = 7.4 \times 10^{-3}$ ; and for **4**:  $J = -237(4) \text{ cm}^{-1}$ ,  $g = 2.21(3)$ ,  $\rho = 0.0163$ ;  $\text{Na} = 149 \times 10^{-6}$  with  $R = 2.4 \times 10^{-3}$ .

### Catecholase Activity

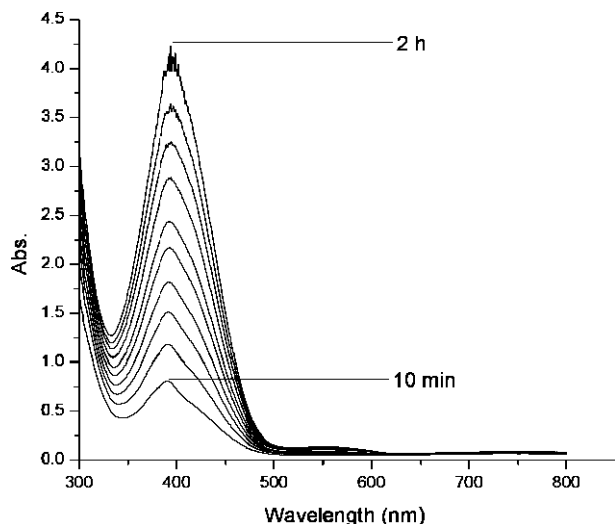
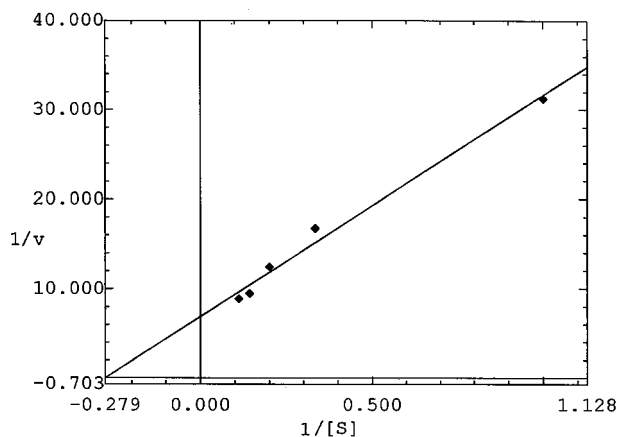
Many copper-containing metalloenzymes, characterized by the dinuclear active site with two copper atoms operating within their convenient intermetallic distance, are involved in distinct processes in living systems among which the type III copper protein catechol oxidase catalyzes the oxidation of a wide range of *ortho*-di-phenols to *ortho*-di-quinones.<sup>[7,8]</sup> Hence, dinuclear copper complexes with two metal atoms in close proximity have received a great deal of attention, particularly in relation to their potential uses as bimetallic catalysts, mimicking the activity of enzymes.<sup>[8,25–27]</sup> Such di-copper(II) complexes exhibiting the catecholase activity are probably crucial for a better understanding of the oxygenation reactions mediated by catechol oxidase.<sup>[28–32]</sup> The  $\text{Cu}^{\text{II}}$  complexes of Schiff-base and reduced Schiff-base ligands studied here have structurally distinct features. Hence we have evaluated their ability to oxidize catechols to quinones by employing 3,5-DTBC, a common and convenient model substrate. Figure 8 shows the course of oxidation of 3,5-DTBC with time in the presence of **4**. The results are shown in Table 4.

A linear relationship between the initial rates and the concentration of the complexes has been obtained for **2–4**, which shows a first-order dependence on the catalyst concentration for these systems. An example of the Lineweaver–Burk plot<sup>[29f]</sup> is given in Figure 9 for **4**. The data obtained from the Lineweaver–Burk plot model is employed for a comparison of catalytic activity.

It is obvious that catalytic ability towards the oxidation of 3,5-DTBC has been found to follow the order: **4** > **2** > **3**. The least activity observed in the case of Schiff-base complex **3** can be attributed to the inefficient binding of the substrate to the catalyst caused by the formation of the

Table 4. Kinetic parameters for the activity of complexes **2–4**.

Complex	$k_{\text{cat}}$ [ $\text{h}^{-1}$ ]	$K_{\text{m}}$ [mM]	$V_{\text{max}}$ [ $10^{-6} \text{ M s}^{-1}$ ]
$[\text{Cu}_2(\text{Sam})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ , <b>2</b> in MeOH	1140 ( $\pm 14$ )	5.4 ( $\pm 0.2$ )	41 ( $\pm 1$ )
$[\text{Cu}_2(\text{Saes})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ , <b>3</b> in MeOH	133 ( $\pm 15$ )	14.3 ( $\pm 0.1$ )	5 ( $\pm 1$ )
$[\text{Cu}_2(\text{Sae})_2] \cdot 2\text{H}_2\text{O}$ , <b>4</b> in MeOH	4612 ( $\pm 28$ )	4.3 ( $\pm 0.1$ )	163 ( $\pm 2$ )
$[\text{Cu}_2(\text{Sae})_2] \cdot 2\text{H}_2\text{O}$ , <b>4</b> in MeOH/ $\text{H}_2\text{O}$ (95:5)	5048 ( $\pm 42$ )	3.2 ( $\pm 0.1$ )	178 ( $\pm 3$ )

Figure 8. Oxidation of 3,5-DTBC by **4** monitored by UV/Vis spectroscopy.Figure 9. Lineweaver–Burk plot for catalysis by **4**.

eight-membered ring with largely separated  $\text{Cu}^{\text{II}}$  ions. Thus, the larger  $\text{Cu} \cdots \text{Cu}$  distance of 5.33 Å in **3** is highly unfavorable for the efficient binding of the substrate. Furthermore, very distinct structural differences between **3** and **4** account for the difference in their activity.

The catecholase activity of copper(II) compounds with different structural parameters has been investigated and compared to some extent by varying the properties of chelating ligands with respect to their conformation, and the number as well as the nature of the donor atoms.<sup>[8]</sup> In our earlier report,<sup>[9]</sup> the reduced Schiff-base complexes  $[\text{Cu}_2(\text{Sab4})_2(\text{H}_2\text{O})_2]$  and  $[\text{Cu}_2(\text{Sbal})_2(\text{H}_2\text{O})_2]$ , containing 4-aminobutanoic acid and 3-aminopropanoic acid ( $\beta$ -alanine)

respectively, were found to exhibit higher activity, which has been attributed to the larger ring size due to a longer alkyl chain in the side arm of the corresponding ligands. It has been proposed that the formation of seven-membered rings in  $[\text{Cu}_2(\text{Sab4})_2(\text{H}_2\text{O})_2]$  and six-membered rings in  $[\text{Cu}_2(\text{Sbal})_2(\text{H}_2\text{O})_2]$  resulted in higher activity, with  $K_{\text{cat}}$  values of 3800 and 1280  $\text{h}^{-1}$  respectively. The lower activity ( $K_{\text{cat}} = 563 \text{ h}^{-1}$ ) in  $[\text{Cu}_2(\text{Sgly})_2(\text{H}_2\text{O})_2]$  due to the shorter glycine side-chain forming five-membered rings appears to support this view. In the present set of complexes, **2** contains aminomethanesulfonate, which is the sulfonic acid analogue of glycine, and **4** has aminoethanesulfonate, which is the sulfonic acid analogue of  $\beta$ -alanine. Based on the connectivity observed in the structures of  $\text{Cu}^{\text{II}}$  complexes containing Schiff bases, as well as chemical, spectroscopic, and catalytic data, the structure of **2** is expected to be similar to that of  $[\text{Cu}_2(\text{Sgly})_2(\text{H}_2\text{O})_2]$ . As a consequence, these five-membered rings formed by the side arm of the ligand in **2** would account for the lower catalytic activity as compared to **4**.

It is important to emphasize here that the  $K_{\text{cat}}$  value of 4612  $\text{h}^{-1}$  observed in **4**, under similar experimental conditions, is much higher than that observed for **2** and **3** and is significantly greater than even the highest activity ( $K_{\text{cat}} = 3800 \text{ h}^{-1}$ ) reported for  $[\text{Cu}_2(\text{Sab4})_2(\text{H}_2\text{O})_2]$ .<sup>[9]</sup> Quite remarkably, complex **4** has also considerably superior catalytic activity compared to its carboxylate analogue  $[\text{Cu}_2(\text{Sbal})_2(\text{H}_2\text{O})_2]$  ( $K_{\text{cat}} = 1287 \text{ h}^{-1}$ ).<sup>[9]</sup> It should be noted that for the five-coordinate dicopper(II) complexes to act as active catalysts, dissociation of the axial bonds should easily occur so that a free coordination site will be readily available for the binding of the substrate in a bridging mode.<sup>[31,32]</sup> A conformationally flexible ligand backbone can easily assist the conformational changes in the dinuclear core and hence the effective binding of the substrate. Compared to the strongly coordinating carboxylate oxygen atoms as in  $[\text{Cu}_2(\text{Sab4})_2(\text{H}_2\text{O})_2]$  or  $[\text{Cu}_2(\text{Sbal})_2(\text{H}_2\text{O})_2]$ , the sulfonate groups are weakly coordinating and can be readily dissociated in solution to accommodate the substrate.<sup>[11,13]</sup> The combined effect of the sufficiently longer alkyl side arm and the weakly coordinating sulfonate donor group facilitate easy binding of the substrate, especially in **4**, and hence enhance its catalytic activity. Further, the presence of a weakly coordinating sulfonate donor group in **2** makes it a more efficient catalyst ( $K_{\text{cat}} = 1140 \text{ h}^{-1}$ ) than its carboxylate analogue  $[\text{Cu}_2(\text{Sgly})_2(\text{H}_2\text{O})_2]$  ( $K_{\text{cat}} = 563 \text{ h}^{-1}$ ).

Our attempts to evaluate the catecholase activity of **2**, **3**, and **4** in pure water have been unsuccessful because of the insolubility of the product 3,5-DTBQ in water. Hence we tried to employ various ratios of MeOH/ $\text{H}_2\text{O}$  in order to investigate the solvent influence on the activity. Nonethe-

less, reliable data could only be collected in 95:5 of MeOH/H<sub>2</sub>O for **4**. From this result, it has been found that the activity of **4** increased by about 10% in the presence of water.

## Summary

Several Cu<sup>II</sup> complexes of the Schiff-base and reduced Schiff-base ligands formed between salicylaldehyde and aminomethane/ethanesulfonic acid have been synthesized and characterized by spectroscopic methods, and the solid-state structures have been determined by X-ray crystallography.

The salient structural features displayed by the Schiff-base copper complexes **1** and **3** provided an opportunity to perform comparative studies with those of the reduced Schiff-base complexes **2** and **4**. Copper centers in **1** and **3** assumed square pyramidal geometry with the apical position preferably occupied by the sulfonate oxygen atoms. While the reduced Schiff-base complexes **4** and **5** form a phenoxo-bridged dinuclear Cu<sub>2</sub>O<sub>2</sub> core with intermetallic distances of 3.03 and 3.06 Å, the Schiff-base complexes **1** and **3** resulted in the formation of eight-membered rings with Cu...Cu distances of 5.12 and 5.33 Å, respectively. Apart from the expected dinuclear copper complexes with a Cu<sub>2</sub>O<sub>2</sub> core, there are also reports of mononuclear copper complexes formed preferentially from Schiff bases containing amino acid residues.<sup>[33]</sup> But strikingly, because of the rigid C=N double bonds, H<sub>2</sub>Sams and H<sub>2</sub>Saes with sulfonic group offered the formation of eight-membered sulfonato-bridged dinuclear copper centers. Furthermore, **1** and **3** generated a hydrogen-bonded 2D structure unlike the 2D (4, 4) coordination polymeric network containing channels in **4**. Recrystallization of **4** in DMF/acetone mixture gave rise to **5** with the solvent DMF coordinated Cu<sup>II</sup> centers. DMF, being a strong coordinating solvent, is able to displace the axial oxygen atoms of sulfonate groups in **4** and convert a (4, 4) net to a 2D hydrogen-bonded structure in **5**.

The crystal structures of **4** and **5** exhibit N–H...O hydrogen bonds from the metal-coordinated imine N–H and the sulfonate O while **1** and **3** illustrate a 2D hydrogen-bonding pattern involving the O(w)–H and sulfonate O atoms. These results will further enhance the structural insight into the transition-metal coordination chemistry of organosulfonates and their derivatives.<sup>[11–13,24]</sup> Variable temperature magnetic studies show that the *syn-syn* sulfonate O–S–O bridges in **3** can mediate antiferromagnetic interaction between Cu<sup>II</sup> ions quite effectively, as well as the expected strong antiferromagnetic coupling through phenoxo bridges in **4**.

While investigating complexes **2–4** as synthetic functional models for the catechol oxidase, **4** has been found to show significantly higher activity than **2** and **3**. Comparative structural studies made between the Schiff-base complexes and the corresponding reduced Schiff-base complexes have provided more insight into the understanding of their catalytic activity. The trend observed in this study using different types of functional groups in the side arm of the li-

gand complements our earlier observation that the ring size of the side arm in these Cu<sup>II</sup> complexes has profound influence on the kinetics of the oxidation of 3,5-DTBC. Further, the complexes described here with a weakly coordinating sulfonate group in the ligands have exhibited higher catecholase activity than that of the corresponding carboxylate analogues with strongly coordinating carboxylate groups. These findings are in agreement with the available data in the literature.<sup>[28–32]</sup>

## Experimental Section

**Materials:** All reagents were purchased from commercial sources and used as received without any further purification.

**Physical Measurements:** The <sup>1</sup>H NMR spectra were recorded with a Bruker ACF300 FT-NMR instrument using TMS as an internal reference by using appropriate deuterated solvents and the IR spectra were recorded using an FTS165 Bio-Rad FTIR spectrometer in the range 4000–450 cm<sup>–1</sup>. The absorption spectra were recorded with a Shimadzu UV-2501/PC UV/Vis spectrophotometer in aqueous solution. ESI-MS spectra were recorded with a Finnigan MAT LCQ mass spectrometer. The elemental analyses were performed in the Microanalytical Laboratory, Department of Chemistry National University of Singapore. Water present in the compounds was determined by an SDT 2960 TGA thermal analyzer with a heating rate of 10 °C min<sup>–1</sup> under nitrogen using a sample size of about 10 mg per run. Variable temperature magnetic studies were made using a Quantum Design MPMS-XL5 SQUID magnetometer operating in an applied field of 5 kOe. The experimental susceptibilities were corrected for the diamagnetism (Pascal's tables).

### Ligand

**N-(2-Hydroxybenzyl)aminoethanesulfonic Acid (H<sub>2</sub>Sae):** Salicylaldehyde (0.29 g, 2.50 mmol) in MeOH (5 mL) was added to a solution of aminoethanesulfonic acid (0.31 g, 2.50 mmol) in MeOH (10 mL) containing NaOH (0.11 g, 2.50 mmol). The yellow solution was stirred for about 45 min at room temperature prior to cooling in an ice bath. The intermediate Schiff base that formed was reduced with an excess of NaBH<sub>4</sub> (0.10 g, 2.65 mmol). The yellow color slowly discharged, and after half an hour the solution was acidified with acetic acid to pH 3–5. Then the solvent was reduced to half and Et<sub>2</sub>O was added to get the product, which was filtered off, washed with Et<sub>2</sub>O, dried, and stored in a desiccator, as H<sub>2</sub>Sae is very hygroscopic. Because of its highly hygroscopic nature, elemental analysis results of H<sub>2</sub>Sae were not consistent and hence are not provided. Yield: 0.35 g (60%). MS (EI): *m/z* (%) = 257.0 [(L<sup>2–</sup> + Na)]. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ = 7.31 and 6.92 ppm (m, 4 H, aromatic), 4.21 (s, 2 H, benzylic –CH<sub>2</sub>), 3.32 (t, 2 H, –CH<sub>2</sub>), 3.21 (t, 2 H, –CH<sub>2</sub>), 2.01 (s, –SO<sub>3</sub>H). <sup>13</sup>C NMR: δ = 157.1 (=C<sub>ar</sub>–O), 115.5 (C<sub>2,ar</sub>), 128.2 (C<sub>3,ar</sub>), 120.8 (C<sub>4,ar</sub>), 129.5 (C<sub>5,ar</sub>), 124.4 (C<sub>6,ar</sub>), 49.4 (–CH<sub>2</sub>SO<sub>3</sub>H), 48.9 (benzylic –CH<sub>2</sub>), 44.0 (–CH<sub>2</sub>CH<sub>2</sub>). IR (KBr): ν̄ = 3365 (OH), 2942 (NH), 1401 and 1115 (SOO<sup>–</sup>), 1030 (SO), 1267 (phenolic CO) cm<sup>–1</sup>.

### Complexes

**[Cu<sub>2</sub>(Sams)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (1):** Salicylaldehyde (0.1 mL, 0.94 mmol) was added to the clear solution containing aminomethanesulfonic acid (0.10 g, 0.94 mmol) and NaOH (0.04 g, 0.94 mmol) in aqueous MeOH (20 mL, 1:1, v/v) to obtain the yellow Schiff base. After stirring for 30 min, copper nitrate trihydrate in MeOH (0.23 g, 0.94 mmol) was directly added in portions and the resulting green product was further stirred for 30 min and filtered, washed with



water, MeOH, Et<sub>2</sub>O and dried under vacuum. Dark green prismatic single crystals suitable for X-ray diffraction were obtained from the filtrate after one day. Yield: 0.2 g (67%). IR (KBr):  $\tilde{\nu}$  = 3400 (OH), 1629 (C=N), 1305 and 1128 (SOO<sup>-</sup>), 1247 (phenolic CO) cm<sup>-1</sup>. UV/Vis (H<sub>2</sub>O):  $\lambda_{\text{max}}$  ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 678 nm (200), 367 nm (13135). MS (ESI):  $m/z$  (%) = 276.7 [CuL]<sup>+</sup>, 553.5 [Cu<sub>2</sub>L<sub>2</sub>]. C<sub>16</sub>H<sub>14</sub>Cu<sub>2</sub>N<sub>2</sub>S<sub>2</sub>O<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub> (589.5): calcd. C 32.6, H 3.1, N 4.7, S 10.9, H<sub>2</sub>O 6.1; found C 32.5, H 3.0, N 4.4, S 10.8, H<sub>2</sub>O 6.8 (from TG weight loss).

**[Cu<sub>2</sub>(Sam)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O (2):** Salicylaldehyde (0.1 mL, 0.94 mmol) in MeCN (10 mL) was added to a clear solution of aminomethanesulfonic acid (0.10 g, 0.94 mmol) and NaOH (0.08 g, 1.88 mmol) in MeOH (10 mL) and the resulting yellow Schiff base solution was stirred for 30 min. The mixture was then cooled in an ice bath followed by the addition of NaBH<sub>4</sub> (0.02 g, 0.47 mmol). The yellow color of the Schiff base slowly discharged after 20 min and the clear solution was maintained at a pH of 4–6 by adding a few drops of CH<sub>3</sub>COOH. Copper nitrate trihydrate (0.23 g, 0.94 mmol) was added to this acidic solution to facilitate in situ complexation. The dark green product obtained after stirring for 1 h was filtered off, washed with MeOH (2 mL), Et<sub>2</sub>O (5 mL), and then dried under vacuum. Yield: 0.22 g (66%). IR (KBr):  $\tilde{\nu}$  = 3450 (OH), 2920 (NH), 1380 and 1147 (SOO<sup>-</sup>), 1037 (SO), 1279 (phenolic CO) cm<sup>-1</sup>. MS (ESI):  $m/z$  (%) = 278.7 [CuL]<sup>+</sup>, 557.8 [Cu<sub>2</sub>L<sub>2</sub>], 580.7 [Cu<sub>2</sub>L<sub>2</sub>Na]<sup>+</sup>. UV/Vis (MeOH)  $\lambda_{\text{max}}$  ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 717 nm (190), 405 nm (870). C<sub>16</sub>H<sub>18</sub>Cu<sub>2</sub>N<sub>2</sub>S<sub>2</sub>O<sub>8</sub>(H<sub>2</sub>O)<sub>3</sub> (611.6): calcd. C 31.4, H 4.0, N 4.7, S 10.5, H<sub>2</sub>O 8.4; found C 31.7, H 4.1, N 4.6, S 10.8, H<sub>2</sub>O 8.0 (from TG weight loss).

**[Cu<sub>2</sub>(Saes)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O (3):** Compound 3 was prepared by a method similar to that described for 1 by using 2-aminoethanesulfonic acid. Yield: 0.2 g (71%). IR (KBr):  $\tilde{\nu}$  = 3443 (OH), 1617 (C=N), 1287 and 1173 (SOO<sup>-</sup>), 1244 (phenolic CO) cm<sup>-1</sup>. UV/Vis (H<sub>2</sub>O):  $\lambda_{\text{max}}$  ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 688 nm (160), 322 nm (5000). C<sub>18</sub>H<sub>18</sub>Cu<sub>2</sub>N<sub>2</sub>S<sub>2</sub>O<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub> (653.6): calcd. C 33.1, H 4.0, N 4.3, S 10.0, H<sub>2</sub>O 11.1; found C 33.3, H 4.1, N 4.4, S 10.1, H<sub>2</sub>O 11.9 (from TG weight loss).

**[Cu<sub>2</sub>(Sae)<sub>2</sub>·2H<sub>2</sub>O (4):** Copper acetate (0.08 g, 0.40 mmol) in MeOH (10 mL) was added to a solution of the ligand H<sub>2</sub>Sae (0.09 g, 0.40 mmol) in MeOH (20 mL) and the resultant solution stirred for about 6 h. The green precipitate formed was filtered, washed with MeOH and Et<sub>2</sub>O, and dried under vacuum. Slow evaporation of the dark green clear aqueous solution of 4 furnished dark green single crystals after 4–5 d. Yield: 0.06 g (55%). IR (KBr):  $\tilde{\nu}$  = 3410 (OH), 2935 (NH), 1312 and 1181 (SOO<sup>-</sup>), 1020 (SO), 1255 (phenolic CO) cm<sup>-1</sup>. UV/Vis (H<sub>2</sub>O):  $\lambda_{\text{max}}$  ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 736 nm (190), 420 nm (855). MS (ESI):  $m/z$  (%) = 291.0 [(CuL)<sup>-</sup>], 522.0 [(CuL<sub>2</sub>)<sup>-</sup>], 584.2 [(Cu<sub>2</sub>L<sub>2</sub>)<sup>-</sup>], 875.0 [(Cu<sub>3</sub>L<sub>3</sub>)<sup>-</sup>], 1106.0 [(Cu<sub>3</sub>-L<sub>4</sub>)<sup>-</sup>], 1397.7 [(Cu<sub>4</sub>L<sub>4</sub>)<sup>-</sup>], 1689.6 [(Cu<sub>5</sub>L<sub>5</sub>)<sup>-</sup>]. C<sub>18</sub>H<sub>22</sub>Cu<sub>2</sub>N<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (H<sub>2</sub>O) (602.18): calcd. C 34.7, H 4.2, N 4.5, S 10.3, H<sub>2</sub>O 5.8; found C 34.3, H 4.2, N 4.6, S 10.3, H<sub>2</sub>O 5.9 (from TG weight loss).

**[Cu<sub>2</sub>(Sae)<sub>2</sub>(DMF)<sub>2</sub>·2DMF (5):** The filtered and clear dark green solution of 4 (0.04 g) in DMF (4 mL) was slowly diffused into acetone (10 mL) in a small beaker. Dark green crystals suitable for the single-crystal X-ray diffraction studies were obtained after a week. Yield: 0.02 g (50%). IR (KBr):  $\tilde{\nu}$  = 2928 (NH), 1387 and 1150 (SOO<sup>-</sup>), 1023 (SO), 1260 (phenolic CO) cm<sup>-1</sup>. UV/Vis (MeOH)  $\lambda_{\text{max}}$  ( $\epsilon$ , M<sup>-1</sup>cm<sup>-1</sup>): 731 nm (195), 412 nm (660). MS (ESI):  $m/z$  (%) = 292.2 [(CuL)<sup>-</sup>], 522.3 [(CuL<sub>2</sub>)<sup>-</sup>], 584.2 [(Cu<sub>2</sub>L<sub>2</sub>)<sup>-</sup>], 875.0 [(Cu<sub>3</sub>L<sub>3</sub>)<sup>-</sup>]. C<sub>30</sub>H<sub>46</sub>Cu<sub>2</sub>N<sub>2</sub>S<sub>2</sub>O<sub>12</sub> (873.9): calcd. C 41.2, H 5.3, N 9.6, S 7.0; found C 41.8, H 5.1, N 9.2, S 7.2.

**Catalytic Activity for the Oxidation of 3,5-DTBC and Kinetic Measurements:** Catecholase activity of complexes for the oxidation of 3,5-DTBC by complexes 2–4 was measured by recording their elec-

tronic spectra at 25 °C by time-dependent UV/Vis spectroscopy. For this purpose, 10<sup>-4</sup> M solutions of complexes 1–4 were treated with 50 equiv. of 3,5-DTBC under aerobic conditions. The UV/Vis spectra of the original solution directly after the addition and after 10, 20, and 30 min were recorded and corrected for volume changes up to 2 h.

The kinetics of oxidation of 3,5-DTBC were measured at 25 °C by the method of initial rates by monitoring the growth of the absorption band at 390 nm of the product 3,5-DTBQ. The complex (2 mg) was added to the 3,5-DTBC solution (25 mL) of concentrations 1.0 × 10<sup>-3</sup>–1.5 × 10<sup>-2</sup> M so that the concentration of the complex was maintained at 10<sup>-4</sup> M. During the first 10 min of the reaction, the development of the absorption band at 390 nm was monitored. In order to determine the kinetic parameters, the Michaelis–Menten approach was applied.<sup>[8,34]</sup>

The reactivity studies were performed in methanol solution because of the good solubility of the substrate, 3,5-DTBC, and of its product 3,5-DTBQ. Also, because of the considerable solubility of 4 in water, investigations have also been attempted in a MeOH/H<sub>2</sub>O mixture for comparison. Attempts to record the activity of 2 and 3 in MeOH/H<sub>2</sub>O were unsuccessful because of the solubility problem producing unreliable data. Preliminary qualitative studies on the activity of 1 have also been unsuccessful owing to its insolubility in common solvents.

**X-ray Crystallography:** The diffraction experiments were carried out on a Bruker AXS SMART CCD diffractometer. The program SMART<sup>[35a]</sup> was used for collecting frames of data, indexing reflection and determination of lattice parameter, SAINT<sup>[35a]</sup> for integration of the intensity of reflections and scaling, SADABS<sup>[35b]</sup> for absorption correction, and SHELXTL<sup>[35c]</sup> for space group and structure determination, least-squares refinements on *F*<sub>2</sub>. Positional and thermal parameters of the non-hydrogen atoms were refined in the least-squares cycles. The hydrogen atom positions and individual *U*s were refined for the water molecules in 1. One of the hydrogen atoms of the lattice water in 3 was found to be disordered. The option DFIX was used in the model to idealize the geometry. No hydrogen atoms could be located for the lattice water in 4. The methyl carbon atom of the lattice DMF was found to be disordered (0.65/0.35) in 5. Only isotropic thermal parameters were refined for the minor component of the disorder.

CCDC-266070 (for 1), CCDC-266071 (for 3), CCDC-266072 (for 4), and CCDC-266073 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see also the footnote on the first page of this article): Molecular and packing diagrams of 5, thermogravimetry of 1–5, UV/Vis plots and Lineweaver–Burk plots for 2–4 (total number of pages: 7).

## Acknowledgments

We gratefully acknowledge the financial support from NUS (R143-000-252-112) and from NSFC (20125104, 20490210).

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Received: July 19, 2005

Published Online: October 17, 2005