

# Interconversion of a Monomer and Two Coordination Polymers of a Copper(II)–Reduced Schiff Base Ligand–1,10-Phenanthroline Complex Based on Hydrogen- and Coordinative-Bonding

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Two compounds,  $[\text{Cu}_3(\text{Sbal})_2(\text{phen})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  (**1**) and  $[\text{Cu}(\text{H}_2\text{Sbal})_2(\text{phen})](\text{ClO}_4)_2$  (**2**), were isolated in successive steps from the reaction mixture containing  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , 1,10-phenanthroline, *N*-(2-hydroxybenzyl)- $\beta$ -alanine ( $\text{H}_2\text{Sbal}$ ), and  $\text{LiOH}$  in the ratio of 1:1:1:1. When the ratio of the base was doubled, the neutral monomer  $[\text{Cu}(\text{Sbal})(\text{phen})] \cdot 2\text{H}_2\text{O}$  (**3**) was obtained. The cation in **1** exists as a one-dimensional polymer in the solid state, while weak O–H $\cdots$ O hydrogen bonds in the cation of **2** generate  $\Delta\Delta\Delta\Delta$  type one-dimensional spiral chains. Addition of  $\text{HClO}_4$  to **3** furnished **1** and **2**, and this mixture can be converted back to **3** by the addition of a base. This conversion of a monomer to two 1-D polymers was found to be reversible. Crystal data for **1**: triclinic space group  $P\bar{1}$ ,  $a = 12.0353(5)$  Å,  $b = 12.2848(5)$  Å,  $c = 15.3185(6)$  Å,  $\alpha = 84.993(1)^\circ$ ,  $\beta = 89.411(1)^\circ$ ,  $\gamma = 67.414(1)^\circ$ ,  $V = 2082.5(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.668$  g cm<sup>-3</sup>. Crystal data for **2**: tetragonal space group  $P4_1/a$ ,  $a = 10.8095(1)$  Å,  $c = 59.0159(4)$  Å,  $V = 6895.7(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.605$  g cm<sup>-3</sup>. Crystal data for **3**: monoclinic space group  $Pn$ ,  $a = 10.6344(3)$  Å,  $b = 5.3953(1)$  Å,  $c = 18.1983(1)$  Å,  $V = 1029.26(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.526$  g cm<sup>-3</sup>. When  $\text{Cu}(\text{NO}_3)_2$  was used in the place of  $\text{Cu}(\text{ClO}_4)_2$ ,  $[\text{Cu}_2(\text{Sbal})(\text{phen})_3](\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (**4**) was the only isolable product for the 1:1:1:1 ratio, and **3** was the only isolable product for the 1:1:1:2 ratio. Crystal data for **4**: triclinic space group  $P\bar{1}$ ,  $a = 10.8063(8)$  Å,  $b = 13.919(1)$  Å,  $c = 16.564(1)$  Å,  $\alpha = 88.957(2)^\circ$ ,  $\beta = 71.008(1)^\circ$ ,  $\gamma = 69.829(2)^\circ$ ,  $V = 2198.9(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.556$  g cm<sup>-3</sup>. Variable temperature magnetic measurements showed that the polymeric structure in **1** behaves, magnetically, as a strongly coupled  $\mu$ -phenoxo dimer ( $2J = -390$  cm<sup>-1</sup>) plus an isolated monomer.

## Introduction

The design of metal-containing building blocks to spontaneously assemble into interesting molecular architectures is of current interest in view of their resemblance to biopolymers as well as their potential applications in materials science.<sup>1,2</sup> Metal coordination polymers are, in general, prepared by self-assembly through the simple mixing of the ligand and the metal ions in a stoichiometric ratio. This molecular self-organization process, operated mainly through weak interactions and dictated by the steric and electronic properties of the molecules, affords only one defined supramolecular species.<sup>3–6</sup> Self-recognition in the formation helicates, for example, was amply described in the literature.<sup>3–6</sup> When mixtures of three or four ligands having varied length of the backbone or the number of coordination sites are added to a suitable metal ion, only homoleptic helicates were formed exclusively, and no mixing of ligands in the

oligomeric species was observed.<sup>7–12</sup> An exciting, yet little explored, area of supramolecular chemistry is the design and synthesis of supramolecules exhibiting switching ability, for example, between monomers and oligomers initiated by the input of external information such as protons, electrons, or photons. In this respect, a pH-dependent reversible self-assembly between a monomer copper complex and oligomer was discovered.<sup>13,14</sup> Lehn and co-workers observed<sup>15</sup> the sequential formation of linear and circular helicate as kinetic and thermodynamic products, respectively. Raymond and co-workers reported<sup>16</sup> the formation of an entropically disfavored tetrahedral

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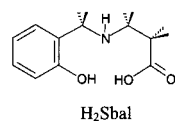
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cluster when a  $\text{Me}_4\text{N}^+$  cation was added to a triple helicate. The pH dependence of the formation of the polymeric structures based on hydrogen-bonding in solution was exemplified by the work of Matsumoto and co-workers.<sup>17–21</sup>

We are interested in the model complexes for the intermediate species in the biological racemization and transamination of amino acids with pyridoxal phosphate. Several copper complexes containing reduced Schiff base ligands between amino acids and salicylaldehyde were found to serve as models.<sup>22</sup> During our attempts to prepare better models, we isolated in successive steps two single-stranded metal-coordination polymers on the basis of hydrogen- and covalent-bonding in the solid state from a mixture of  $\text{Cu}(\text{ClO}_4)_2$ , *N*-(2-hydroxybenzyl)- $\beta$ -alanine ( $\text{H}_2\text{Sbal}$ ), and 1,10-phenanthroline (phen). These strands are found to be interconvertible to the monomer by the addition of phen and of a base, whereas the monomer can be converted back to two 1-D polymers by the addition of aqueous  $\text{HClO}_4$ . This paper describes the results of our investigations in detail.



## Experimental Section

All materials were obtained commercially and were used as received. The yields are reported with respect to the metal salts. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker ACF300FT-NMR machine using TMS as an internal reference at 25 °C in  $\text{D}_2\text{O}$ , and the IR spectra (KBr pellet) were recorded using an FTS165 Bio-Rad FTIR spectrophotometer. The electronic transmittance spectra were recorded on a Shimadzu UV-2501/PC UV-vis spectrophotometer using Nujol mulls and in MeOH solution. Room-temperature magnetic susceptibility measurements were carried out at a Johnson-Matthey magnetic susceptibility balance with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the standard. Corrections for diamagnetism were made using Pascal's constants. The reported magnetic moments are per  $\text{Cu}^{\text{II}}$  ion. Variable temperature magnetic measurements were made using a Quantum Design MPMS 5 Squid magnetometer operating in an applied field of 1 T. The powdered sample was contained in a calibrated gelatine capsule which was held in the center of a drinking straw, with the straw attached to the end of the sample rod. The temperature and the field calibrations were checked against a standard palladium sample, supplied by Quantum Design, and were checked against  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Conductance measurements were made using a Kyoto Electronics CM-115 conductivity meter using 1 mM solutions. ESI-MS spectra were recorded on a Finnigan MAT LCQ mass spectrometer. The elemental analyses were performed in the microanalytical laboratory, chemistry department, National University of Singapore. Water present in the compounds was determined by using an SDT 2980 TGA thermal analyzer with a heating rate of 10 °C  $\text{min}^{-1}$  in a  $\text{N}_2$  atmosphere using a sample size of 5–10 mg per run. *Caution! Perchlorate salts are potentially dangerous as explosives and should only be handled in small quantities, although we worked with these  $\text{ClO}_4^-$  salts without any incident.*

**Ligand,  $\text{H}_2\text{Sbal}$ .** To a solution of  $\beta$ -alanine (0.89 g, 10 mmol) and KOH (0.56 g, 10 mmol) in 10 mL of MeOH was added salicylaldehyde

(1.20 g, 10 mmol) in 10 mL of MeOH. The yellow solution was stirred for 2 h at room temperature prior to cooling in an ice bath. The intermediate Schiff base that formed was reduced with an excess of  $\text{NaBH}_4$  (0.46 g, 12 mmol) in MeOH containing a few drops of NaOH solution. The yellowish color was slowly discharged, the solution was evaporated after 10 min and was extracted with dry MeOH, and then the solution was acidified with concentrated HCl to a pH of 5.0–6.0. The resulting colorless solid was filtered off, washed with dry MeOH and  $\text{Et}_2\text{O}$ , dried, and recrystallized from  $\text{H}_2\text{O}/\text{EtOH}$  (1:1). Yield: 0.92 g (47%); mp 205–206 °C. Anal. Calcd for  $\text{C}_{10}\text{H}_{13}\text{N}_1\text{O}_3 \cdot \text{H}_2\text{O}$ : C, 56.34; H, 7.04; N, 6.57. Found: C, 56.43; H, 6.97; N, 6.38.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  2.60 (t, 2H,  $J = 6.6$  Hz), 3.24 (t, 2H,  $J = 6.6$  Hz), 4.25 (d, 2H), 6.94–6.99 (m, 2H), 7.34–7.40 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ ): 173.1 (C=O), 156.3 ( $\text{C}_1$ -Ar), 129.4 ( $\text{C}_5$ -Ar), 128.5 ( $\text{C}_3$ -Ar), 120.9 ( $\text{C}_6$ -Ar), 117.9 ( $\text{C}_4$ -Ar), 114.9 ( $\text{C}_2$ -Ar), 47.1 ( $\text{C}_4$ ), 43.4 ( $\text{C}_3$ ), 32.2 ( $\text{C}_2$ ). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$  3425;  $\nu(\text{NH})$  3060,  $\nu(\text{COO}^-)$  1595, 1464,  $\nu(\text{phenolic, CO})$  1270.

**Reaction between  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , Phen,  $\text{H}_2\text{Sbal}$ , and LiOH in the Ratio of 1:1:1:1.** An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.371 g, 1.00 mmol) was added to a MeOH solution (10 mL) of 1,10-phenanthroline, phen (0.180 g, 1.00 mmol). To this mixture was added  $\text{H}_2\text{Sbal}$  (0.200 g, 1.00 mmol) along with LiOH (1 mL, 1 M). The dark green solution was stirred for 2 h, filtered, and left for several days to get dark green prismatic crystals of **1** which were separated by filtration and were air-dried. Yield: 0.092 g (35%). After the green crystals were filtered from the above experiment, the solution was left for a week, and dark blue rhombohedral crystals of **2** were obtained which were isolated by filtration and dried in air. Yield: 0.079 g (38%). Compounds **1** and **2** were also isolated as described below in moderate yield.

The compound  $[\text{Cu}_2(\text{Sbal})(\text{phen})_3](\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (**4**) was obtained as the only isolable product from the reaction of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , phen,  $\text{H}_2\text{Sbal}$ , and LiOH in the ratio of 1:1:1:1. Compound **4** was also synthesized in moderate yield when the reaction was repeated with the correct stoichiometry as described below.

**$[\text{Cu}_2(\text{Sbal})_2(\text{phen})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , **1**.** An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.278 g, 0.75 mmol) was added to a MeOH solution (10 mL) of phen (0.045 g, 0.25 mmol), and the resultant solution was added slowly to an aqueous solution containing  $\text{H}_2\text{Sbal}$  (0.100 g, 0.5 mmol) and LiOH (1.0 mL, 1 M). The dark green solutions were stirred for 4 h with gentle heating, filtered, and left for several days which provided green prism-like crystals of **1** which were separated by filtration and air-dried. Yield: 0.181 g (69%). Anal. Calcd for  $\text{C}_{32}\text{H}_{40}\text{N}_4\text{O}_{19}\text{Cl}_2\text{Cu}_3$ : C, 37.02; H, 3.80; N, 5.45;  $\text{H}_2\text{O}$ , 8.6. Found: C, 36.70; H, 3.82; N, 5.35;  $\text{H}_2\text{O}$ , 8.5. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$  3420,  $\nu(\text{NH})$  2925,  $\nu(\text{COO}^-)$  1588 and 1427,  $\nu(\text{phenolic, CO})$  1279,  $\nu(\text{Cl-O})$  1179 and 1089.

**$[\text{Cu}(\text{H}_2\text{Sbal})_2(\text{phen})](\text{ClO}_4)_2$ , **2**.** To the solution formed from  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.185 g, 0.5 mmol) in 10 mL of water and phen (0.90 g, 0.5 mmol) in 10 mL of MeOH was added dropwise  $\text{H}_2\text{Sbal}$  (0.200 g, 1.00 mmol) without base. The blue solution was stirred for 4 h with gentle heating, filtered, and left for several days, and dark blue rhombohedral crystal of **2** were obtained which were isolated by filtration and air-dried. Yield: 0.254 (61%). Anal. Calcd for  $\text{C}_{32}\text{H}_{34}\text{N}_4\text{O}_{14}\text{Cl}_2\text{Cu}$ : C, 46.44; H, 4.00; N, 6.81. Found: C, 46.10; H, 4.08; N, 6.72. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{NH})$  2919,  $\nu(\text{COO}^-)$  1607 and 1389,  $\nu(\text{phenolic, CO})$  1271,  $\nu(\text{Cl-O})$  1119 and 1086.

**$[\text{Cu}(\text{Sbal})(\text{phen})] \cdot 2\text{H}_2\text{O}$ , **3**.** To the blue solution formed from  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.371 g, 1.00 mmol) in 15 mL of MeOH and phen (0.180 g, 1.00 mmol) in 10 mL of MeOH was added an aqueous methanolic solution (10 mL, 50% v/v) of  $\text{H}_2\text{Sbal}$  (0.200 g, 1.00 mmol) with LiOH (2.0 mL, 1 M solution). The dark green solution was stirred for 2 h, filtered, and left for crystallization. Yellow-green crystals were separated by decantation, washed with EtOH, and dried in vacuo. Yield: 0.350 g (74%). Anal. Calcd for  $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_5\text{Cu}$ : C, 55.47; H, 4.57; N, 8.64;  $\text{H}_2\text{O}$ , 7.6. Found: C, 55.81; H, 4.86; N, 8.89;  $\text{H}_2\text{O}$ , 7.6. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$  3424,  $\nu(\text{NH})$  3119,  $\nu(\text{COO}^-)$  1596 and 1478,  $\nu(\text{phenolic, CO})$  1284.

Under the same experimental conditions mentioned above, **3** was obtained exclusively when  $\text{NO}_3^-$  or  $\text{CH}_3\text{CO}_2^-$  was used in the place of  $\text{ClO}_4^-$  salt.

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**Table 1.** Crystal Data and Structure Refinement Details

	1	2	3	4
formula	C <sub>32</sub> H <sub>40</sub> Cl <sub>2</sub> Cu <sub>3</sub> N <sub>4</sub> O <sub>19</sub>	C <sub>32</sub> H <sub>34</sub> Cl <sub>2</sub> CuN <sub>4</sub> O <sub>14</sub>	C <sub>22</sub> H <sub>23</sub> CuN <sub>3</sub> O <sub>5</sub>	C <sub>46</sub> H <sub>40</sub> Cu <sub>2</sub> N <sub>9</sub> O <sub>11.5</sub>
formula weight	1046.20	833.07	472.97	1029.95
temp, K	293(2)	293(2)	223(2)	293(2)
wavelength, λ/Å	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	tetragonal	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 4 <sub>1</sub> / <i>a</i>	<i>Pn</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	12.0353(5)	10.8095(1)	10.6344(3)	10.8063(8)
<i>b</i> /Å	12.2848(5)	10.8095(1)	5.3953(1)	13.9194(11)
<i>c</i> /Å	15.3185(6)	59.0159(4)	18.1983(1)	16.5636(13)
α/°	84.993(1)	90	90	88.957(2)
β/°	89.411(1)	90	99.686(1)	71.008(1)
γ/°	67.414(1)	90	90	69.829(2)
<i>V</i> /Å <sup>3</sup>	2082.5(2)	6895.7(1)	1029.26(4)	2198.9(3)
<i>Z</i>	2	8	2	2
<i>d</i> (calcd)/g cm <sup>-3</sup>	1.668	1.605	1.526	1.556
μ/mm <sup>-1</sup>	1.727	0.865	1.102	1.043
reflns collected	10287	17403	4954	10237
independent reflns	6865	3046	2588	4961
<i>R</i> <sub>int</sub>	0.040	0.033	0.031	0.0737
GOF	1.045	1.069	1.009	1.056
final <i>R</i> [ <i>I</i> > 2σ( <i>I</i> )], <i>R</i> <sub>1</sub> <sup>a</sup>	0.0803	0.0645	0.0291	0.0719
w <i>R</i> <sub>2</sub> <sup>a</sup>	0.1775	0.1669	0.0567	0.1722

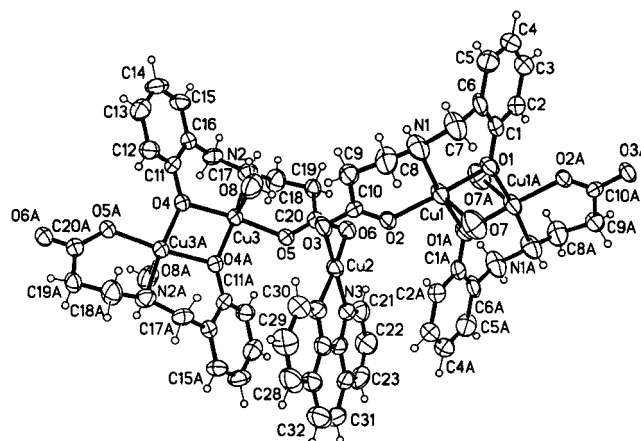
$$^a R_1 = (||F_o| - |F_c||)/(|F_o|); wR_2 = [(w(F_o^2 - F_c^2))/(wF_o^4)]^{1/2}.$$

[Cu<sub>2</sub>(Sbal)(phen)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, **4**. To a dark green solution formed from Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.242 g, 1.00 mmol) in water (10 mL) and phen (0.270 g 1.5 mmol) in 10 mL of MeOH was added a solution of H<sub>2</sub>Sbal (0.100 g, 0.50 mmol) in aqueous MeOH (20 mL, 50% v/v) with LiOH (1.0 mL, 1 M). The dark green solution was stirred for 2 h, filtered, and left for slow evaporation to provide dark green crystals which were isolated by filtration and air-dried. Yield: 0.36 g (69%). Anal. Calcd for C<sub>46</sub>H<sub>40</sub>N<sub>9</sub>O<sub>11.5</sub>Cu<sub>2</sub>: C, 53.37; H, 4.03; N, 11.98; H<sub>2</sub>O, 4.5. Found: C, 53.64; H, 3.89; N, 12.24; H<sub>2</sub>O, 4.4. IR (KBr, cm<sup>-1</sup>): ν(OH) 3419; ν(NH) 3057; ν(COO<sup>-</sup>) 1625 and 1384; ν(phenolic, CO) 1279.

**X-ray Crystallography.** The diffraction experiments were carried out on a Bruker AXS SMART CCD diffractometer. The program SMART<sup>23</sup> was used for collecting frames of data, for indexing reflection, and for the determination of lattice parameters; SAINT<sup>23</sup> was used for integration of the intensity of reflections and scaling; SADABS<sup>24</sup> was used for absorption correction; and SHELXTL<sup>25</sup> was used for space group and structure determination and for least-squares refinements on *F*<sup>2</sup>. Of the three water molecules found in the lattice of **1**, two were disordered with occupancies of 0.5 each, and no hydrogen atom was added to these disordered water molecules. The oxygen atoms of the ClO<sub>4</sub><sup>-</sup> in **2** were found to be severely disordered. In the major model with occupancy of 0.7, two different orientations were found for three oxygen atoms and were related by 3-fold rotation along the O—Cl bond. The positional and isotropic thermal parameters of all of the hydrogen atoms were refined in **3**. The two NO<sub>3</sub><sup>-</sup> anions in **4** were disordered. Two triangular oxygen models were included for one nitrate anion (occupancy, 0.65 and 0.35), and two independent orientations of NO<sub>3</sub><sup>-</sup> with occupancies of 0.75 and 0.25 were modeled for the second disordered nitrate anion. Isotropic thermal parameters were refined for each disorder model. The leftover electron densities were assigned to the oxygen atoms of 2.5 H<sub>2</sub>O molecules in six different places in the lattice. Selected crystallographic data and refinement details are displayed in Table 1.

## Results and Discussion

Green prismatic crystals of [Cu<sub>3</sub>(Sbal)<sub>2</sub>(phen)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O (**1**) were isolated from a dark green solution containing



**Figure 1.** Thermal ellipsoids plot diagram of the repeating unit of the cationic polymer in **1**.

a mixture of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, H<sub>2</sub>Sbal, and LiOH in the ratio of 1:1:1. The filtrate furnished dark blue rhombohedral crystals of [Cu(H<sub>2</sub>Sbal)<sub>2</sub>(phen)](ClO<sub>4</sub>)<sub>2</sub> (**2**) within a week. When the ratio of the base was doubled, the expected neutral monomeric compound, [Cu(Sbal)(phen)]·2H<sub>2</sub>O (**3**) was obtained as yellow-green crystals in quantitative yield. Compounds **1**, **2**, and **3** were characterized by X-ray crystallography. Compounds **1** and **2** were also synthesized from the stoichiometric ratios of Cu<sup>II</sup> salt, H<sub>2</sub>Sbal, and phen ligands and base in quantitative yield.

When the reaction was repeated with Cu(NO<sub>3</sub>)<sub>2</sub> instead of Cu(ClO<sub>4</sub>)<sub>2</sub>, [Cu<sub>2</sub>(Sbal)(phen)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (**4**) was the only product isolated for the 1:1:1:1 ratio of the reactants; however, this is not the only product of the reaction. When the green filtrate was evaporated, a mixture of green, blue, and white solids was obtained. In any case, the products of this reaction were different from that of employing ClO<sub>4</sub><sup>-</sup> anions. The reaction with a 1:1:1:2 ratio gave exclusively **3**.

**Description of Structures.** The building blocks of the 1-D polymeric cation in **1** are composed of a dimer, [Cu<sub>2</sub>(Sbal)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>], and [Cu(phen)]<sup>2+</sup> fragments as depicted in Figure 1. The two copper centers in the dimer have distorted square pyramidal geometry with the base comprised of two tridentate dianionic Sbal ligands with bridging phenolate groups similar

(23) SMART & SAINT Software Reference manuals, Version 5.0; Bruker AXS Inc.: Madison, WI, 1998.

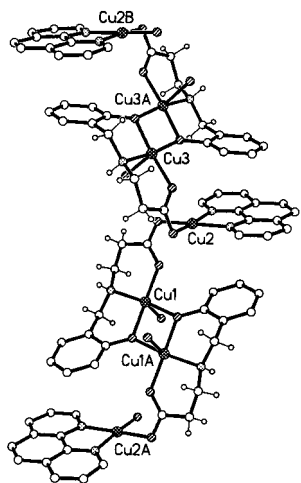
(24) Sheldrick, G. M. SADABS software for empirical absorption correction; University of Gottingen: Germany, 1996.

(25) SHELXTL Reference manual, Version 5.1; Bruker AXS Inc.: Madison, WI, 1998.

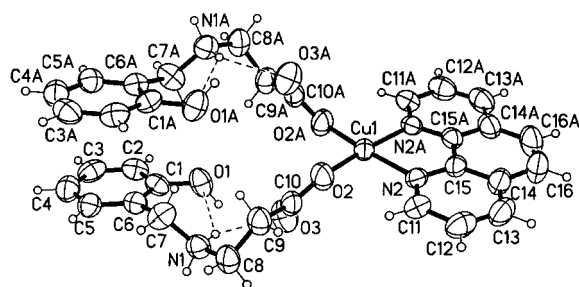
**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1**

Cu(1)—O(1)	1.943(6)	C(9)—C(10)	1.504(12)	O(1)—Cu(1)—O(2)	164.9(3)	C(8)—N(1)—Cu(1)	111.4(7)
Cu(1)—O(2)	1.947(5)	C(10)—O(2)	1.249(9)	O(1)—Cu(1)—O(1) <sup>a</sup>	79.0(2)	C(7)—N(1)—Cu(1)	106.9(6)
Cu(1)—O(1) <sup>a</sup>	1.954(6)	C(10)—O(3)	1.262(9)	O(2)—Cu(1)—O(1) <sup>a</sup>	93.5(2)	N(1)—C(8)—C(9)	115.2(10)
Cu(1)—N(1)	2.007(8)	O(3)—Cu(2)	1.953(6)	O(1)—Cu(1)—N(1)	94.1(3)	C(8)—C(9)—C(10)	115.8(8)
Cu(1)—O(7)	2.362(7)	Cu(2)—N(4)	1.983(7)	O(2)—Cu(1)—N(1)	92.4(3)	O(2)—C(10)—O(3)	120.4(8)
Cu(1)—Cu(1) <sup>a</sup>	3.006(2)	Cu(2)—N(3)	1.987(7)	O(1) <sup>a</sup> —Cu(1)—N(1)	172.4(3)	O(2)—C(10)—C(9)	122.5(8)
O(1)—C(1)	1.361(10)	Cu(2)—O(6)	2.007(6)	O(1)—Cu(1)—O(7)	89.3(3)	O(3)—C(10)—C(9)	117.2(8)
O(1)—Cu(1) <sup>a</sup>	1.954(6)	O(4)—C(11)	1.368(9)	O(2)—Cu(1)—O(7)	104.0(2)	C(10)—O(2)—Cu(1)	129.4(5)
C(1)—C(2)	1.386(13)	O(4)—Cu(3)	1.939(5)	O(1) <sup>a</sup> —Cu(1)—O(7)	90.8(3)	C(10)—O(3)—Cu(2)	113.1(5)
C(1)—C(6)	1.396(13)	O(4)—Cu(3) <sup>b</sup>	1.953(5)	N(1)—Cu(1)—O(7)	92.5(3)	O(3)—Cu(2)—N(4)	91.3(3)
C(2)—C(3)	1.390(13)	N(2)—Cu(3)	1.999(7)	O(1)—Cu(1)—Cu(1) <sup>a</sup>	39.66(17)	O(3)—Cu(2)—N(3)	174.0(3)
C(3)—C(4)	1.347(16)	C(20)—O(6)	1.244(9)	O(2)—Cu(1)—Cu(1) <sup>a</sup>	131.57(18)	N(4)—Cu(2)—N(3)	83.4(3)
C(4)—C(5)	1.368(16)	C(20)—O(5)	1.273(9)	O(1) <sup>a</sup> —Cu(1)—Cu(1) <sup>a</sup>	39.38(16)	O(3)—Cu(2)—O(6)	91.6(2)
C(5)—C(6)	1.418(14)	O(5)—Cu(3)	1.933(6)	N(1)—Cu(1)—Cu(1) <sup>a</sup>	133.7(2)	N(4)—Cu(2)—O(6)	173.5(3)
C(6)—C(7)	1.471(14)	Cu(3)—O(4) <sup>b</sup>	1.953(5)	O(7)—Cu(1)—Cu(1) <sup>a</sup>	90.1(2)	N(3)—Cu(2)—O(6)	93.9(3)
C(7)—N(1)	1.528(12)	Cu(3)—O(8)	2.380(7)	C(1)—O(1)—Cu(1)	124.5(5)	C(11)—O(4)—Cu(3)	118.9(5)
N(1)—C(8)	1.404(12)	Cu(3)—Cu(3) <sup>b</sup>	2.993(2)	C(1)—O(1)—Cu(1) <sup>a</sup>	131.1(6)	C(11)—O(4)—Cu(3) <sup>b</sup>	133.5(5)
C(8)—C(9)	1.463(13)			Cu(1)—O(1)—Cu(1) <sup>a</sup>	101.0(2)	Cu(3)—O(4)—Cu(3) <sup>b</sup>	100.5(2)
				C(18)—N(2)—C(17)	114.2(7)	O(5)—Cu(3)—N(2)	92.9(3)
				C(18)—N(2)—Cu(3)	112.5(6)	O(4)—Cu(3)—N(2)	94.7(3)
				C(17)—N(2)—Cu(3)	109.8(5)	O(4) <sup>b</sup> —Cu(3)—N(2)	170.3(3)
				N(2)—C(18)—C(19)	113.0(8)	O(5)—Cu(3)—O(8)	89.9(3)
				C(18)—C(19)—C(20)	117.0(7)	O(4)—Cu(3)—O(8)	89.0(3)
				O(6)—C(20)—O(5)	119.9(8)	O(4) <sup>b</sup> —Cu(3)—O(8)	94.6(3)
				O(6)—C(20)—C(19)	119.3(7)	N(2)—Cu(3)—O(8)	93.1(3)
				O(5)—C(20)—C(19)	120.8(8)	O(5)—Cu(3)—Cu(3) <sup>b</sup>	132.6(2)
				C(20)—O(5)—Cu(3)	128.3(5)	O(4)—Cu(3)—Cu(3) <sup>b</sup>	39.9(2)
				C(20)—O(6)—Cu(2)	102.5(5)	O(4) <sup>b</sup> —Cu(3)—Cu(3) <sup>b</sup>	39.6(2)
				O(5)—Cu(3)—O(4)	172.3(2)	N(2)—Cu(3)—Cu(3) <sup>b</sup>	134.2(2)
				O(5)—Cu(3)—O(4) <sup>b</sup>	93.1(2)	O(8)—Cu(3)—Cu(3) <sup>b</sup>	92.3(2)
				O(4)—Cu(3)—O(4) <sup>b</sup>	79.5(2)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $-x, -y + 1, -z + 1$ . <sup>b</sup> Symmetry transformations used to generate equivalent atoms:  $-x + 1, -y + 1, -z$ .

**Figure 2.** A view of the packing of the 1-D polymeric cations in **1**.

to the dimers previously reported.<sup>26,27</sup> Water completes the coordination sphere in the apical sites on each Cu<sup>II</sup> in an anti configuration. The two free carbonyl groups of the Sbal ligands further link the “Cu(phen)” moieties along the strand to furnish a one-dimensional polymer as depicted in Figure 2. The coordination geometry around this third Cu<sup>II</sup> is, therefore, square planar and has a CuN<sub>2</sub>O<sub>2</sub> core. All of the polymers are arranged parallel along the [101] direction with a pitch of 19.383 Å. Selected bond distances and angles are given in Table 2. The dimers bonded to “Cu(phen)” fragments are crystallographically independent, and each dimer has a crystallographic center of

**Figure 3.** Molecular structure of the cation in **2** showing the numbering scheme and hydrogen-bonding.

inversion at the center of the Cu<sub>2</sub>O<sub>2</sub> parallelogram. In the dimer, the phenolic oxygen atoms O(1) and O(4) are asymmetrically bridging the Cu<sup>II</sup> atoms. The C—O distances at C(10) and C(20) are not equal which indicates that the carboxylate anions are not delocalized. Hence, it may be concluded that the carbonyl oxygen atoms O(3) and O(6) are bonded to Cu(3). The two longer apical Cu—O bonds (distances, 2.362(7) and 2.380(7) Å) are due to a Jahn–Teller distortion.

The N—H protons are involved in weak hydrogen-bonding to the water molecules in the lattice. One of the hydrogens attached to the aqua oxygen O(8) is involved in strong intramolecular hydrogen-bonding to O(3). The hydrogen-bonding parameters are as follows: O(8)—H(82), 0.85 Å; H(82)···O(3), 2.018 Å; O(8)—H(82)···O(3), 150.8°; O(8)—O(3), 2.789 Å. The other O—H and N—H hydrogen atoms are involved in weak to strong hydrogen-bonding to the top oxygen atoms of the lattice water molecules. However, no interesting patterns were observed.

Figure 3 shows a perspective view of the [Cu(H<sub>2</sub>Sbal)<sub>2</sub>(phen)]<sup>2+</sup> cation in **2** that consists of a Cu<sup>II</sup>, a bidentate phenolic ligand, and two H<sub>2</sub>Sbal ligands. The oxygen atoms of the

(26) Ranford, J. D.; Vittal, J. J.; Wu, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 1114.

(27) Ranford, J. D.; Vittal, J. J.; Wu, D.; Yang, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3498.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **2**

Cu(1)–O(2)	1.922(3)	C(8)–C(9)	1.503(7)	O(2)–Cu(1)–O(2) <sup>a</sup>	97.8(2)	O(3)–C(10)–O(2)	126.4(5)
Cu(1)–O(2) <sup>a</sup>	1.922(3)	C(9)–C(10)	1.519(7)	O(2)–Cu(1)–N(2)	90.3(2)	O(3)–C(10)–C(9)	118.4(4)
Cu(1)–N(2)	2.008(3)	C(10)–O(3)	1.235(6)	O(2) <sup>a</sup> –Cu(1)–N(2)	171.6(2)	O(2)–C(10)–C(9)	115.2(5)
Cu(1)–N(2) <sup>a</sup>	2.008(3)	C(10)–O(2)	1.266(6)	N(2)–Cu(1)–N(2) <sup>a</sup>	81.6(2)	C(10)–O(2)–Cu(1)	125.2(4)
O(1)–C(1)	1.372(6)	N(2)–C(11)	1.324(6)	C(2)–C(1)–O(1)	122.7(4)	C(11)–N(2)–C(15)	118.6(4)
C(1)–C(2)	1.370(7)	N(2)–C(15)	1.352(5)	C(2)–C(1)–C(6)	120.5(5)	C(11)–N(2)–Cu(1)	128.6(3)
C(1)–C(6)	1.401(6)	C(11)–C(12)	1.408(7)	O(1)–C(1)–C(6)	116.7(4)	C(15)–N(2)–Cu(1)	112.8(3)
C(2)–C(3)	1.378(8)	C(12)–C(13)	1.353(8)	C(1)–C(2)–C(3)	119.5(5)	N(2)–C(11)–C(12)	121.7(5)
C(3)–C(4)	1.370(8)	C(13)–C(14)	1.409(8)	C(4)–C(3)–C(2)	121.3(5)	C(13)–C(12)–C(11)	119.8(5)
C(4)–C(5)	1.376(7)	C(14)–C(15)	1.401(6)	C(3)–C(4)–C(5)	118.8(5)	C(12)–C(13)–C(14)	120.0(5)
C(5)–C(6)	1.381(7)	C(14)–C(16)	1.426(8)	C(4)–C(5)–C(6)	121.5(5)	C(15)–C(14)–C(13)	116.5(5)
C(6)–C(7)	1.515(7)	C(15)–C(15) <sup>a</sup>	1.421(9)	C(5)–C(6)–C(1)	118.3(4)	C(15)–C(14)–C(16)	118.2(5)
C(7)–N(1)	1.468(6)	C(16)–C(16) <sup>a</sup>	1.34(1)	C(5)–C(6)–C(7)	122.1(4)	C(13)–C(14)–C(16)	125.3(5)
N(1)–C(8)	1.488(6)			C(1)–C(6)–C(7)	119.3(4)	N(2)–C(15)–C(14)	123.4(4)
				N(1)–C(7)–C(6)	113.7(4)	N(2)–C(15)–C(15) <sup>a</sup>	116.4(2)
				C(7)–N(1)–C(8)	113.6(4)	C(14)–C(15)–C(15) <sup>a</sup>	120.2(3)
				N(1)–C(8)–C(9)	115.1(4)	C(16) <sup>a</sup> –C(16)–C(14)	121.6(3)
				C(8)–C(9)–C(10)	114.4(4)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $-x, -y + 3/2, z$ .

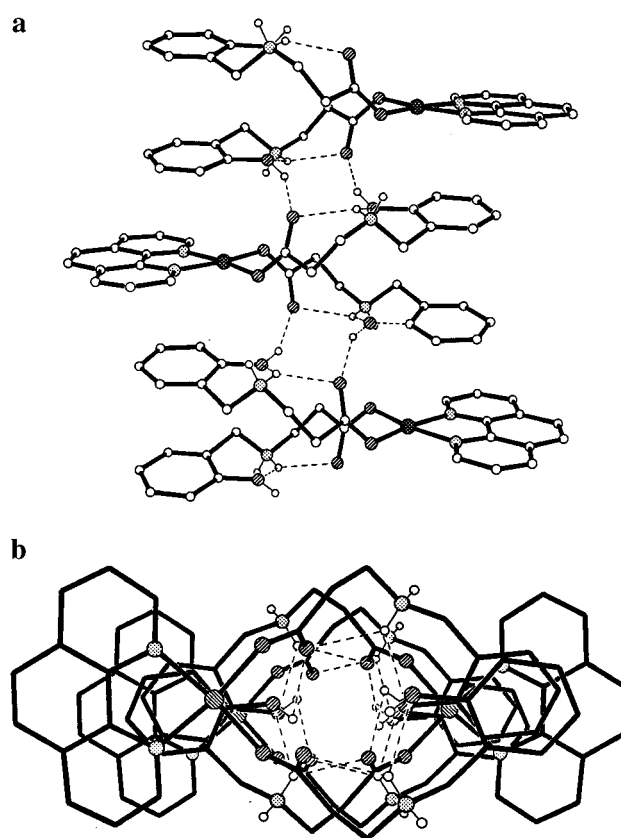
**Table 4.** Hydrogen Bond Distances (Å) and Angles (deg) in **2**

D–H	<i>d</i> (D–H)	<i>d</i> (H···A)	∠DHA	<i>d</i> (D···A)	A	symmetry
O1–H1	0.88	2.374	121.6	3.091	O3	[ <i>x</i> , <i>y</i> – 0.5, – <i>z</i> ]
N1–H1A	0.90	2.119	129.3	2.778	O1	
N1–H1A	0.90	2.173	128.5	2.822	O3	
N1–H1B	0.90	2.066	160.5	2.930	O6	[– <i>x</i> + 1, – <i>y</i> + 2, – <i>z</i> ]
N1–H1B	0.90	2.073	148.0	2.876	O8	[– <i>x</i> + 1, – <i>y</i> + 2, – <i>z</i> ]
N1–H1B	0.90	2.211	131.5	2.887	O5A	[– <i>x</i> + 1, – <i>y</i> + 2, – <i>z</i> ]
N1–H1B	0.90	2.570	144.4	3.343	O4A	[– <i>x</i> + 1, – <i>y</i> + 2, – <i>z</i> ]

carboxylate groups from H<sub>2</sub>Sbal ligands are bonded in *cis* fashion to give a square planar geometry for Cu<sup>II</sup> similar to that found in **1**. The Cu(1)–O(2) distance, 1.922(3) Å, is shorter than those found in **1** for Cu(2). A closer look at the geometrical parameters around C(10) in Table 3 would indicate that Cu<sup>II</sup> is bonded to C–O<sup>−</sup> and not to the carbonyl oxygen atom of CO<sub>2</sub><sup>−</sup> ion as found in **1**. This is reflected in a slightly longer Cu–N distance (2.008(3) Å) as compared to the Cu–N distances (Cu(2)–N(3), 1.987(7) Å and Cu(2)–N(4), 1.983(7) Å) observed in **1**.

The carboxylic acid is deprotonated by the amine of the H<sub>2</sub>Sbal to form a zwitterion. The carbonyl oxygen atoms and the protons of the phenolic and of the –NH<sub>2</sub><sup>+</sup> groups of the H<sub>2</sub>Sbal ligands are involved in extensive hydrogen-bonding. More specifically, one of the –NH<sub>2</sub><sup>+</sup> hydrogen atoms is bonded intramolecularly to phenolic and carboxylic carbonyl oxygen atoms, while the second hydrogen atom is involved in N–H···O bonding with ClO<sub>4</sub><sup>−</sup> ions. The phenolic protons are weakly hydrogen bonded to the top C=O groups in the neighboring cations to generate one-dimensional ΔΛΔΛ.. type spiral chains as illustrated in Figure 4a, and the spiral structure is evident when viewed from the spiral axis (Figure 4b). Table 4 displays relevant hydrogen-bonding parameters. These chains do not pass through any crystallographic axes and are aligned parallel to each other in *ab* planes, and the direction of propagation of the chains alternates in *a* and *b* axes along the *c*-direction in the cell.

Compound **3** crystallized in noncentrosymmetric space group, *Pn*. The structure of **3** consists of a neutral monomer [Cu(Sbal)(phen)], in which the Cu<sup>II</sup> has an approximate square pyramidal geometry as shown in Figure 5. The four basal positions are occupied by two N atoms of the phen ligand and by phenolic O and amine N atoms of the Sbal ligand. The coordination sphere at the apical position is completed by the carboxylate O atom of the ligand. Selected bond distances and angles are listed in Table 5. It is interesting to note that in a similar neutral



**Figure 4.** (a) A segment of the hydrogen-bonded spiral (ΔΛΔΛ.. type) polymer cation in **2**. Only the hydrogens involved in hydrogen-bonding are shown. (b) Top view of the polymer cation **2** showing the presence of spiral structure.

monomer, [Cu(Sala)(phen)]·H<sub>2</sub>O, although it has the same square pyramidal molecular geometry, the square base is occupied by the atoms from Sala and by one of the N atoms of the phen.<sup>22</sup> The structure of **3** may be viewed as a geometrical isomer of [Cu(Sala)(phen)]·H<sub>2</sub>O in which an –NH–CH(CH<sub>3</sub>)–CO<sub>2</sub> fragment is replaced by an –NH–CH<sub>2</sub>–CH<sub>2</sub>–CO<sub>2</sub> moiety which reflects the influence of ring expansion on the geometry. In **3**, the two Cu–N distances (2.093(3) and 2.029(3) Å) from the phen ligand are quite similar, whereas they are not similar in the Sala derivative since each N atom occupies axial and equatorial positions.<sup>22</sup> For the same reason, the two Cu–O distances in the Sala derivative are equal but are not equal in **3**.

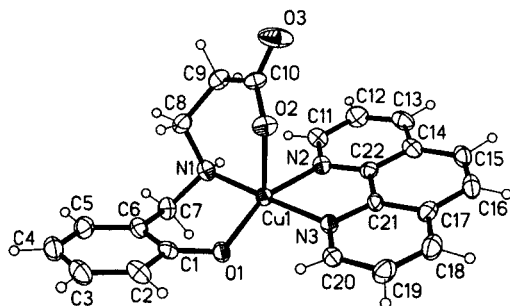


Figure 5. A perspective view of the neutral monomer **3**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **3**

Cu(1)–O(1)	1.938(2)	O(3)–C(10)	1.247(5)
Cu(1)–N(1)	2.006(3)	N(1)–C(7)	1.491(5)
Cu(1)–N(3)	2.029(3)	N(1)–C(8)	1.497(6)
Cu(1)–N(2)	2.093(3)	N(2)–C(11)	1.351(5)
Cu(1)–O(2)	2.185(3)	N(2)–C(22)	1.355(5)
O(1)–C(1)	1.334(5)	N(3)–C(20)	1.320(5)
O(2)–C(10)	1.268(5)	N(3)–C(21)	1.371(5)
O(1)–Cu(1)–N(1)	93.38(13)	C(7)–N(1)–C(8)	110.6(3)
O(1)–Cu(1)–N(3)	88.99(12)	C(7)–N(1)–Cu(1)	112.5(3)
N(1)–Cu(1)–N(3)	177.15(15)	C(8)–N(1)–Cu(1)	112.5(3)
O(1)–Cu(1)–N(2)	157.70(11)	C(11)–N(2)–C(22)	116.9(3)
N(1)–Cu(1)–N(2)	96.94(14)	C(11)–N(2)–Cu(1)	130.7(3)
N(3)–Cu(1)–N(2)	80.30(13)	C(22)–N(2)–Cu(1)	111.8(3)
O(1)–Cu(1)–O(2)	110.65(11)	C(20)–N(3)–C(21)	117.9(3)
N(1)–Cu(1)–O(2)	91.93(12)	C(20)–N(3)–Cu(1)	128.2(3)
N(3)–Cu(1)–O(2)	88.72(11)	C(21)–N(3)–Cu(1)	113.5(3)
N(2)–Cu(1)–O(2)	88.75(11)	O(1)–C(1)–C(2)	120.6(4)
C(1)–O(1)–Cu(1)	124.1(3)	O(1)–C(1)–C(6)	121.5(4)
C(10)–O(2)–Cu(1)	123.5(2)		

Table 6. Hydrogen Bond Distances (Å) and Angles (deg) in **3**

D–H	<i>d</i> (D–H)	<i>d</i> (H···A)	∠DHA	<i>d</i> (D···A)	A	symmetry
N1–H1	0.77	2.152	145.1	2.822	O2	[ <i>x</i> , <i>y</i> – 1, <i>z</i> ]
O1S–H1SA	0.89	1.847	160.0	2.706	O3	[ <i>x</i> + 1/2, – <i>y</i> + 1, <i>z</i> – 1/2]
O1S–H1SB	0.89	2.023	170.7	2.905	O2S	[ <i>x</i> , <i>y</i> + 1, <i>z</i> ]
O2S–H2SA	0.90	1.877	173.7	2.775	O1	
O2S–H2SB	0.90	1.990	167.9	2.873	O1S	

Two highly ordered water molecules present in the lattices generate an interesting hydrogen-bonding network in the solid state. The N–H and all of the H atoms of the water molecules participate in hydrogen-bonding. Selected H-bonding interactions are displayed in Table 6. The N–H proton hydrogen bonds to O(2) which forms a chain along the *b* axis. One of the H atoms from each water molecule in the lattice is hydrogen bonded to each other which forms an O–H···O chain along the *b* axis parallel to the N–H···O bonds. The other hydrogen atom from each water molecule strongly hydrogen bonded to the O(1) and to the O(3) of the Sbal ligand which forms a two-dimensional sheet as shown in Figure 6.

Compound **4** is a dimer in which the [Cu(Sbal)(phen)] monomer is bonded to the [Cu(phen)<sub>2</sub>]<sup>2+</sup> cation through the oxygen atom of the delocalized CO<sub>2</sub><sup>–</sup> group in the Sbal ligand as shown in Figure 7. The [Cu(Sbal)(phen)] fragment has square pyramidal geometry around Cu<sup>II</sup>, and the geometric parameters listed in Table 7 are comparable to **3**. However, the conformation of the ligand backbone is quite different from **3**. For example, the phenolic aromatic ring is approximately in plane with the phen ligand in **3**, while it is perpendicular to the phen ring in **4**. The flexible backbone of the Sbal ligand allows the Cu<sup>II</sup> complexes to have different conformations in these complexes. In the second fragment, Cu(2) also has a distorted square pyramidal geometry with a CuN<sub>4</sub>O core from the three

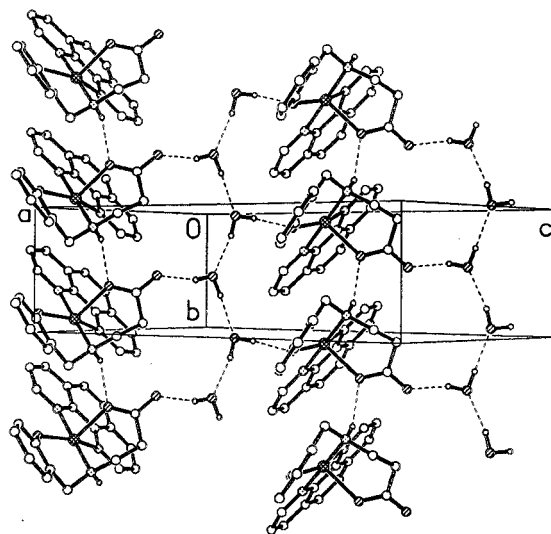


Figure 6. Hydrogen-bonding between **3** and the water molecules in the crystal lattice.

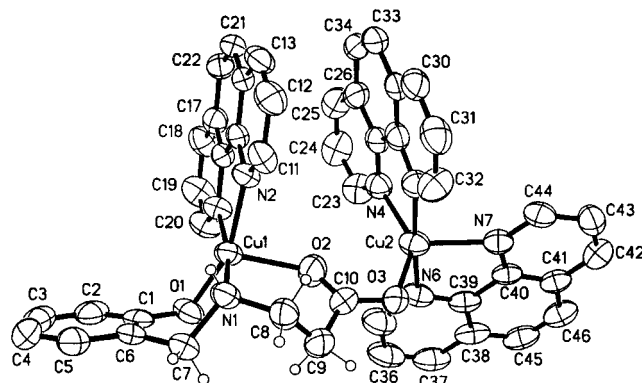


Figure 7. ORTEP diagram showing the labeling scheme in **4**.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **4**

Cu(1)–O(1)	1.948(4)	Cu(2)–N(6)	2.000(5)
Cu(1)–N(3)	2.025(5)	Cu(2)–N(4)	2.092(6)
Cu(1)–N(1)	2.031(5)	Cu(2)–N(7)	2.162(6)
Cu(1)–N(2)	2.095(5)	O(1)–C(1)	1.332(8)
Cu(1)–O(2)	2.141(5)	C(10)–O(2)	1.251(8)
Cu(2)–N(5)	1.991(5)	C(10)–O(3)	1.255(8)
Cu(2)–O(3)	1.997(5)		
O(1)–Cu(1)–N(3)	89.5(2)	O(3)–Cu(2)–N(6)	92.0(2)
O(1)–Cu(1)–N(1)	91.3(2)	N(5)–Cu(2)–N(4)	81.2(2)
N(3)–Cu(1)–N(1)	168.2(2)	O(3)–Cu(2)–N(4)	140.0(2)
O(1)–Cu(1)–N(2)	159.8(2)	N(6)–Cu(2)–N(4)	97.0(2)
N(3)–Cu(1)–N(2)	80.7(2)	N(5)–Cu(2)–N(7)	95.6(2)
N(1)–Cu(1)–N(2)	94.7(2)	O(3)–Cu(2)–N(7)	111.4(2)
O(1)–Cu(1)–O(2)	104.5(2)	N(6)–Cu(2)–N(7)	80.2(2)
N(3)–Cu(1)–O(2)	94.9(2)	N(4)–Cu(2)–N(7)	108.5(2)
N(1)–Cu(1)–O(2)	96.3(2)	C(1)–O(1)–Cu(1)	110.2(4)
N(2)–Cu(1)–O(2)	94.0(2)	O(1)–C(1)–C(2)	122.1(7)
N(5)–Cu(2)–O(3)	92.6(2)	C(10)–O(2)–Cu(1)	123.8(5)
N(5)–Cu(2)–N(6)	174.7(2)	C(10)–O(3)–Cu(2)	110.6(4)

N atoms of the two phen ligands and the carbonyl O atom to occupy the square base and the fourth nitrogen atom N(7) at the apical site. The carboxylate of Sbal is delocalized as inferred from the C(10)–O distances, 1.251(8) and 1.255(8) Å. The presence of strong  $\pi\cdots\pi$  interactions between the two phen ligands attached to each Cu<sup>II</sup> atom is evident as they are bent toward each other with an interplanar angle of 15.2°. Hence, the interplanar distances are minimum at the peripheral. The closest C···C distance, 3.177 Å, is between C(21) and C(34). The internuclear Cu···Cu separation is 4.775(1) Å.

**Table 8.** Electronic Absorption, Conductivity, and Magnetic Data for 1–4

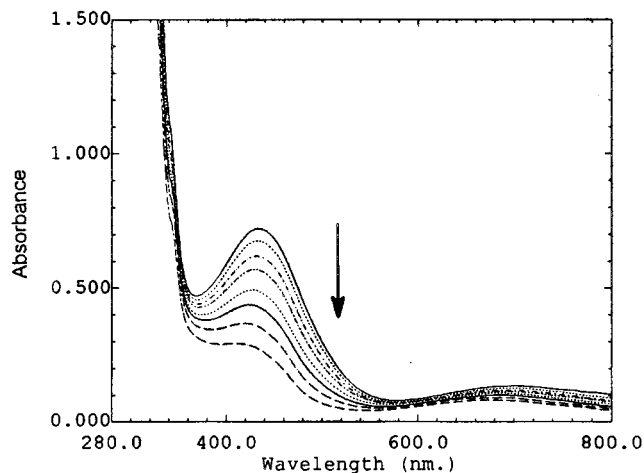
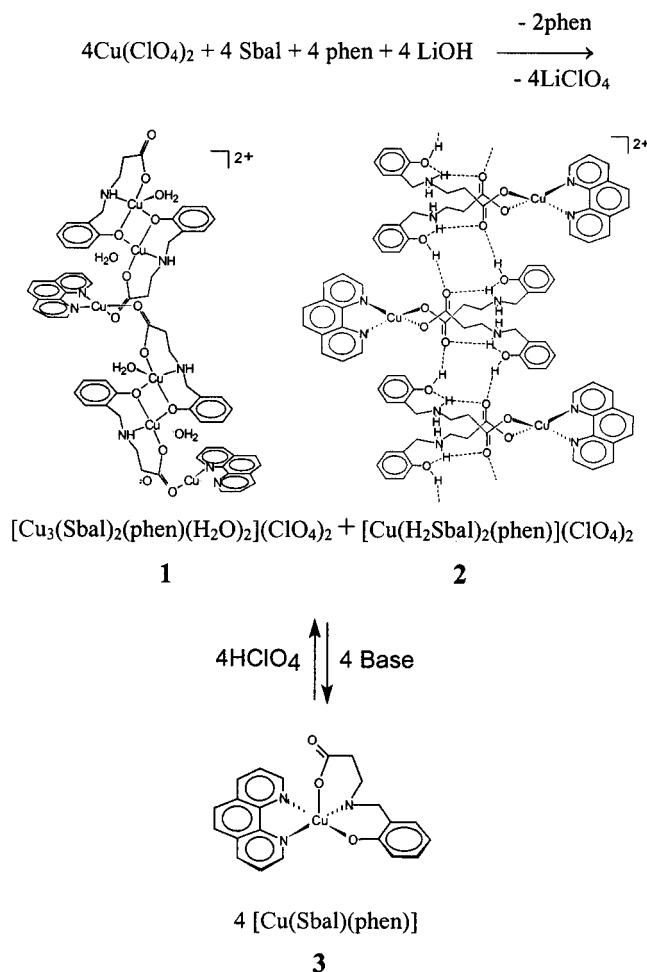
complex	absorption bands (nm) <sup>a</sup>		molar conductivity <sup>d</sup> S cm <sup>-2</sup> mol <sup>-1</sup>	magnetic moment $\mu_B$
	CT	d–d		
<b>1</b>	385 (1180)	665 (200) <sup>b</sup>	94	1.37
	400 sh	680 br <sup>c</sup>		
<b>2</b>	400 (220)	655(120) <sup>b</sup>	103	1.79
	360 sh	600 br <sup>c</sup>		
<b>3</b>	430(720)	705 (140) <sup>b</sup>	3	1.78
	460 sh	680 br <sup>c</sup>		
<b>4</b>	430 (670)	690 (160) <sup>b</sup>	111	1.50
	400 sh	700 br <sup>c</sup>		

<sup>a</sup>  $\lambda_{\max}$  ( $\epsilon$ ). <sup>b</sup> In MeOH. <sup>c</sup> As Nujol mull transmittance. <sup>d</sup> In DMSO.

**Physicochemical Studies.** Electronic spectral data in MeOH solution and as Nujol mulls are given in Table 8 along with molar conductivity and room-temperature magnetic data. The UV absorption band observed in MeOH solution at 385 nm in **1** is assigned to the CT band from the ligands Sbal and phen to the Cu<sup>II</sup> transition, whereas the band at 400 nm is due to the  $\pi^*-\pi$  transition of phen to Cu<sup>II</sup> in **2**. It should be noted that the phenolate moiety of the Sbal ligand is not bonded to Cu<sup>II</sup> in **2**. The d–d transition band at 665 nm may be assigned to the square planar CuN<sub>2</sub>O<sub>2</sub> and the square pyramidal CuN<sub>1</sub>O<sub>4</sub> chromophores in **1**, and at 655 nm it is due to the square planar CuN<sub>2</sub>O<sub>2</sub> chromophore in **2**. The absorption band at 430 nm for **3** is assigned to the charge transfer from Sbal and phen to the Cu<sup>II</sup> transition. The d–d transition band at 705 nm in **3** may be assigned to the square pyramidal CuN<sub>2</sub>O<sub>3</sub> chromophore. The square pyramidal Cu<sup>II</sup> in **3** has its ligand field transition at a longer wavelength as compared to **2**.<sup>28</sup> The mull transmittance spectra for **1–4** exhibit essentially two bands, and the assignments of the electronic transitions are similar to those discussed above. The changes in the numerical values observed in MeOH solution may be attributed to solvent effects. The molar conductance values in DMSO indicate that **1**, **2**, and **4** are 1:2 electrolytes, and **3** is a nonelectrolyte.

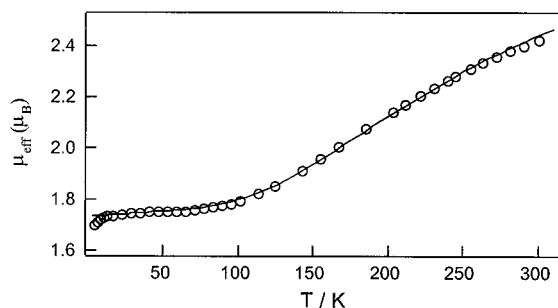
With the addition of NaOH base to the 1:1:1:1 mixture of Cu(ClO<sub>4</sub>)<sub>2</sub>, phen, H<sub>2</sub>Sbal, and LiOH, the intensity of an absorption band at ~410 nm increased and slightly red shifted to ~440 nm. The increase in the intensity of this CT transition can be attributed to the formation of the terminal phenolate bonding to Cu<sup>II</sup>. The intensity of the d–d transition band at ca. 670 nm increases to 700 nm, while the intensity of absorption maxima shifted only a very little. The shift in the d–d band to lower energy may be attributed to a change in the coordination geometries from a mixture of square planar in **1** and **2** and square pyramid in **1** to the pure square pyramid with N<sub>3</sub>O<sub>2</sub> mode in **3**. The formation of monomer **3** in the resultant solution was further confirmed by comparing the electronic spectra of pure **3** in MeOH and by subsequent isolation of **3** from the solution. The changes in the UV–vis spectra of **3** by the incremental addition of (HClO<sub>4</sub>) shown in Figure 8 indicate that the formation of (the repeating units in) **1** and **2** is reversible and indicate the absence of any isobestic point. The latter appears to imply that all of the Cu<sup>II</sup> chromophores in **1–3** absorb in the same narrow region of the spectrum concerned in the solution. However, this result demonstrates that the interconversion between the monomer and the two polymers **1** and **2** is reversible as depicted in Scheme 1.

The electronic spectrum of the solution containing **1**, **2**, and phen in a 1:1:2 ratio resembles the mixture containing Cu-

**Figure 8.** Variation of the UV–vis spectra for the monomer **3** with addition of aqueous HClO<sub>4</sub>.**Scheme 1**

(ClO<sub>4</sub>)<sub>2</sub>, phen, H<sub>2</sub>Sbal, and LiOH in the ratio 1:1:1:1. This observation confirms the presence of the chromophores and the coordination geometries around the copper atoms in **1** and **2**. However, it does not prove the existence of two polymeric species in MeOH solution. ESI mass spectra were recorded for **1–3** to investigate the existence of the polymeric structures of **1** and **2** in MeOH solution. The ESI mass spectra of **1** and **2** indicate the presence of various dissociated species in solution such as [Cu(Sbal)(phen)+H]<sup>+</sup>, [Cu(phen)<sub>3</sub>]<sup>2+</sup>, [Cu<sub>2</sub>(Sbal)<sub>2</sub>+H]<sup>+</sup>, [Cu<sub>3</sub>(Sbal)<sub>3</sub>+H]<sup>+</sup>, etc. for **1**, and [Cu(HSbal)(phen)]<sup>+</sup>, [Cu-

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**Figure 9.** Plots of  $\mu_{\text{eff}}$  ( $\mu_{\text{B}}$ ) per  $\text{Cu}_3$  for complex **1**. The solid lines are calculated using a dimer plus isolated monomer model<sup>30</sup> with  $g(\text{dimer}) = 2.0$ ,  $g(\text{monomer}) = 2.0$ ,  $N\alpha = 180 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ , and  $J = -195 \text{ cm}^{-1}$ .

(phen)<sub>3</sub>]<sup>2+</sup>, H<sub>2</sub>Sbal, etc. for **2** (Supporting Information). Interestingly, the molecular ion peaks corresponding to [Cu(Sbal)(phen)+H]<sup>+</sup> and [Cu(phen)<sub>3</sub>]<sup>2+</sup> were observed for the neutral monomeric **3**. It is clear that these polymeric species are not stable in solution. Only a few polymeric species were characterized in solution.<sup>29</sup> An ESI spectrum of the mixture containing Cu(ClO<sub>4</sub>)<sub>2</sub>, phen, H<sub>2</sub>Sbal, and LiOH in the ratio 1:1:1:1 also shows the presence of various dissociated species, which confirms that these two polymeric cations **1** and **2** do not exist in solution.

The  $\mu_{\text{eff}}$  values for **2** and **3** (Table 8) are normal for uncoupled Cu(II). However, the depressed magnetic moment for **1**, 1.37  $\mu_{\text{B}}$ , indicates moderately strong antiferromagnetic coupling occurs for this complex which has two independent Cu(II) dimers with a metal–metal separation of 3.006(2) and 2.993(2) Å. A lower magnetic moment for **4** in which the two Cu(II) centers are separated by 4.775 Å is attributed to weak antiferromagnetic coupling. Magnetic susceptibilities were measured for complex **1** over the temperature range 4.2–300 K in an applied field of 1 T and are shown in Figure 9. The corresponding magnetic moments are also shown and decrease from 2.41  $\mu_{\text{B}}$  per  $\text{Cu}_3$  (1.39  $\mu_{\text{B}}$  per Cu) at 300 K to a plateau of 1.75  $\mu_{\text{B}}$  between 100 and 10 K, then a small but rapid decrease to 1.69  $\mu_{\text{B}}$  at 4.2 K occurs. This behavior is indicative of medium strength antiferromagnetic coupling yielding a spin doublet,  $S = 1/2$ , ground state responsible for the plateau. The magnetic data were analyzed by fitting the susceptibilities to an equation calculated using a  $-2J\mathbf{S}_1 \cdot \mathbf{S}_2$  Hamiltonian for a dimer plus isolated monomer model.<sup>30</sup> The parameters have their usual meanings;  $N\alpha$  was set at  $180 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for the  $\text{Cu}_3$  moiety. In Figure 9, we see that a very good fit was obtained with  $g_1 = g_2 = 2.0$

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and  $J = -195 \text{ cm}^{-1}$ . The crystallographically independent dimeric units could not be distinguished magnetically. The  $J$  value is typical for a  $\mu$ -phenoxo-bridged planar moiety having a Cu–O–Cu angle of 100° and a Cu··Cu distance of 3 Å. The coupling between the dinuclear moiety in the chain and the Cu(phen) group is negligible, as expected, because of both the anti-syn carboxylate bridging mode and the orthogonal relationship of the planes of the Cu(phen)(O)<sub>2</sub> and the Cu<sub>2</sub>O<sub>2</sub> groups. Use of other trinuclear models such as a scalene triangle<sup>30,31</sup> gave no improvement compared to the dimer plus monomer model described above.

## Summary

By changing the metal–ligand ratio, the counterions, and the pH of the solution, four new compounds were synthesized and were characterized in the solid state as well as in solution. In the absence of any self-recognition component embedded in the ligand, two different types of 1-D polymers viz. a hydrogen-bonded spiral polymer and metal coordination polymer with different metal-to-ligand composition were produced taking advantages of the different locations of the binding sites of the ligand Sbal, a second ancillary chelating phen ligand, and the ability of Cu<sup>II</sup> to have variable coordination geometry. These two polymers were isolated in successive steps which implies a change of the solution composition and reaction conditions during the course of isolation. Although UV–vis titration results appear to support the formation of the expected chromophores in solution, ESI mass spectral data indicate that these polymers do not exist in MeOH solution. In any case, the formation of two different polymers from a monomer appears to be novel and has not been observed before. Further, these two supramolecular complexes were shown to form a monomer by the addition of phen and a base. The two metal coordination polymers can be isolated from the reaction mixture by the addition of HClO<sub>4</sub> to the monomer. This proton-dependent interconversion between the monomer and the two polymers was found to be reversible. Several such pH-dependent reversible self-assembly systems are known,<sup>12,13,16–20</sup> but only one supramolecule was the exclusive product.

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**Supporting Information Available:** ESI-MS patterns and UV–vis spectra along with X-ray crystallographic files in CIF format for complexes **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC010479B

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