Model for the Reduced Schiff Base Intermediate between Amino Acids and Pyridoxal: Copper(II) Complexes of *N*-(2-Hydroxybenzyl)amino Acids with Nonpolar Side Chains and the Crystal Structures of [Cu(*N*-(2-hydroxybenzyl)-D,L-alanine)(phen)]·H_2O and [Cu(*N*-(2-hydroxybenzyl)-D,L-alanine)(imidazole)]

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Copper(II) complexes with reduced Schiff base ligands of amino acids possessing nonpolar side chains with salicylaldehyde have been synthesized. Ternary complexes with imidazole, 1,10-phenanthroline, and pyridine have been prepared and characterized for *N*-(2-hydroxybenzyl)-D,L-alanine. The crystal structures of [(*N*-(2-hydroxybenzyl)-D,L-alanine)(1,10-phenanthroline)Cu(II)] monohydrate ([Cu(SAla)phen]·H_2O) and [(*N*-(2-hydroxybenzyl)-D,L-alanine)(imidazole)Cu(II)] ([Cu(SAla)Him]), have been determined. [Cu(SAla)phen]·H_2O crystallized in space group $P\bar{1}$, with $a = 8.718(2)$ Å, $b = 10.886(3)$ Å, $c = 11.693(2)$ Å, $\alpha = 71.32(2)°$, $\beta = 85.27(2)°$, $\gamma = 70.21(2)°$, and $Z = 2$. The copper atom is five coordinate, with SAla acting as a tridentate ONO chelator through the carboxylato and phenolato oxygens and the amine nitrogen. The remaining donors are provided by the phen nitrogens. [Cu(SAla)Him] crystallized in space group $P2_1/n$, with $a = 10.353(1)$ Å, $b = 6.714(1)$ Å, $c = 18.769(2)$ Å, $\beta = 91.71(1)°$, and $Z = 4$. The copper atom is four coordinate, with SAla acting as a tridentate ONO chelator with the neutral imidazole moiety coordinated through nitrogen. In both complexes the ligand has two chiral centers due to the coordination of the N. Molecular mechanics calculations show that unfavorable steric interactions would occur in the nonobserved *R*,*R* and *S*,*S* diastereomers. Compounds prepared have been characterized by a range of physicochemical techniques. The complexes may serve as stable models for the intermediates in enzymatic amino acid transformations.

Introduction

Considerable attention has been given to Schiff base adducts formed between pyridoxal or analogs and amino acids.[1,2] Pyridoxal phosphate (PLP) is a cofactor required by many enzymes catalyzing transformations that amino acids undergo.[3] For example, transamination and racemization reactions involve the formation of an intermediate Schiff base,[4] hemoglobin will react with PLP to form a Schiff base,[5] and PLP-dependent enzymes are involved in α-, *β*-, and *γ*-elimination reactions of amino acids.[4,6,7] Both metal ions and H^+ increase the rate of such reactions,[8,9] although enzymatic reactions appear to use only H^+.[9] Metals do, however, catalyze pyridoxal-mediated reactions of amino acids in model systems, with copper(II) showing the highest activity.[10] Research has tended to focus on copper(II) complexes of *N*-salicylideneglycine,[11] with imidazole, pyrazole, related derivatives, and pyridine ternary adducts being investigated by ESR[12] and for their redox properties.[13]

The reaction mechanisms proposed are mainly derived from model studies of amino acids with pyridoxal or related Schiff bases and their metal complexes. Spectroscopic evidence shows that there is often marginal formation of Schiff base in the absence of a transition metal.[6] In fact, a metal is typically required in model studies both as a template and to stabilize the resulting product.[1c,14] X-ray crystal structures of complexes

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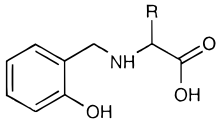
show the ligand to act as a tridentate moiety, coordinating through the phenolato O, imine N, and carboxyl O.[15] With histidine, the possibility of imidazole complexation also exists.[10,16] The stability of the Schiff base products isolated depends on factors such as the amino acid side chain polarity,[6] the metal, pH, solvent, and temperature.[9] However, racemic complexes are often observed even when optically active amino acids are employed.[2,6,15i] Transamination, decomposition, hydrolysis of amino acid esters, ester exchange, and oxidation reactions have been observed as well.[2] Casella and Gullotti found that Schiff bases between amino acids with nonpolar side chains and 2-formylpyridine were unstable with Zn(II) and Cu(II), and only imines of histidine or its methyl ester could be isolated in reasonable purity.[6]

The problems with ligand instability can be overcome by reduction of the Schiff base to give an amine, and this presents interesting possibilities. Ligands are now more flexible and not constrained to remaining planar. They may also model the intermediates in transamination reactions where addition of a nucleophilic solvent across the double bond is thought to occur.[2] Although the role of copper has been stressed, to date only solution studies measuring the stability constants of nonisolated complexes have been determined for chiral ligands.[17] As it has been suggested that ternary adduct formation may play a role in the *in vivo* activity of complexes through binding of the species to biological ligands, it is of interest to investigate these. The only crystal structures for this ligand type appear to be the cobalt ternary complex[18] [α-*N*-(*o*-hydroxybenzyl)-L-histidinato]-(L-alaninato)cobalt(III) dihydrate ([Co(SHis)Ala]·2H_2O) and the Gly derivatives[19] [{Cu(SGly)}$_2$(H_2O)]·H_2O and [Co(NH_3)$_6$]-[Co(SGly)$_2$]$_2$Cl.

In this paper we have prepared reduced Schiff base ligands of salicylaldehyde with glycine (H_2SGly, R = H), alanine (H_2SAla, R = CH_3), leucine [H_2SLeu, R = $CH_2CH(CH_3)_2$], isoleucine [H_2SIle, R = $CH(CH_3)CH_2CH_3$], phenylalanine (H_2SPhe, R = $CH_2C_6H_5$), and glycine methyl ester (HSGlyMe).



Binary and ternary copper(II) complexes of these have been isolated and characterized, and the single-crystal X-ray structures of the ternary adducts [Cu(SAla)phen]·H_2O and [Cu(SAla)Him] have been determined. Molecular mechanics calculations have been used to show the preference for the *S*,*R* and *R*,*S* configurations at the Cα and amine N centers found in the complexed ligands. We highlight the differences between the structural and spectroscopic properties of our complexes and related classical Cu(II) Schiff base−amino acid systems studied as models in enzymatic amino acid transformations.

Experimental Section

Ligand Preparations. To a solution of the appropriate amino acid (10 mmol) in water (10 cm^3) containing KOH (0.56 g, 10 mmol) was added salicylaldehyde (1.20 g, 10 mmol) in ethanol (10 cm^3). The yellow solution was stirred for 30 min at room temperature prior to cooling in an ice bath. The intermediate Schiff base that had formed was reduced with an excess of sodium borohydride (0.46 g, 12 mmol) in water (5 cm^3) containing a few drops of sodium hydroxide solution. The yellow color slowly discharged, and after 10 min the solution was acidified with concentrated HCl to a pH of 3.5−5.0. The resulting solid was filtered off, washed with ethanol and then diethyl ether, dried, and recrystallized from water/ethanol (1:1).

H_2SGly: yield, 49%; mp 210−11 °C (lit.[20] mp 210−12 °C); ^{1}H NMR [$(CD_3)_2SO$] δ 3.14 (s, 2H), 3.97 (s, 2H), 6.77−6.86 (m, 2H), 7.15−7.24 (m, 2H). Anal. Calcd(Found): C, 59.7(59.7); H, 6.2(6.1); N, 7.6(7.7).

H_2SAla: yield, 40%; mp 241−2 °C; ^{1}H NMR [$(CD_3)_2SO$] δ 1.30 (d, 3H, J = 7.1 Hz), 3.24 (q, 1H, J = 7.1 Hz), 3.88 and 4.00 (AB system, 2H, J_{AB} = 13.5 Hz), 6.76−6.83 (m, 2H), 7.14−7.24 (m, 2H). Anal. Calcd(Found): C, 61.6(61.5); H, 6.6(6.7); N, 7.2(7.2).

H_2SLeu·0.5H_2O: yield, 57%; mp 222−3 °C; ^{1}H NMR [$(CD_3)_2SO$] δ 0.83 (d, 3H, J = 6.6 Hz), 0.87 (d, 3H, J = 6.6 Hz), 1.54−1.42 (m, 1H), 1.81−1.73 (m, 2H), 3.15 (t, 1H, J = 7.1 Hz), 3.78 and 3.94 (AB system, 2H, J_{AB} = 13.6 Hz), 6.75−6.80 (m, 2H), 7.12−7.20 (m, 2H). Anal. Calcd(Found): C, 64.1(64.1); H, 8.0(8.2); N, 5.6(5.8).

H_2SIle: yield, 56%; mp 219−21 °C; ^{1}H NMR [$(CD_3)_2SO$] δ 0.82 (t, 3H, J = 7.4 Hz), 0.86 (d, 3H, J = 6.8 Hz), 1.36 (m, 2H), 1.71 (m, 1H), 3.02 (d, 1H, J = 3.8 Hz), 3.71 and 3.92 (AB system, 2H, J_{AB} = 13.6 Hz), 6.73−6.78 (m, 2H), 7.09−7.17 (m, 2H). Anal. Calcd-(Found): C, 65.7(65.8); H, 8.0(8.0); N, 5.9(5.9).

H_2SPhe·H_2O: yield, 86%; mp 211−2 °C; ^{1}H NMR [$(CD_3)_2SO$] δ 2.97 (d, 2H, J = 6.9 Hz), 3.42 (t, 1H, J = 6.9 Hz), 3.61 and 3.79 (AB system, 2H, J_{AB} = 13.6 Hz), 6.70−6.74 (m, 2H), 6.99−7.11 (m, 2H), 7.21−7.31 (m, 5H). Anal. Calcd(Found): C, 66.8(65.8); H, 6.2(6.6); N, 5.0(4.8).

***N*-(2-Hydroxybenzyl)glycine Methyl Ester (HSGlyMe).** A solution of salicylaldehyde (0.90 cm^3, 7.5 mmol) and glycine methyl ester·HCl (0.95 g, 7.5 mmol) in methanol (15 cm^3) with methanolic KOH (1 M, 7.5 cm^3) was mixed and stirred at room temperature for 30 min. The reaction was then cooled in an ice bath, and sodium borohydride (0.46 g, 12 mmol) was added in several portions. After 15 min of stirring the pH was adjusted to 5 with acetic acid. The solvent was evaporated under reduced pressure and water was added. After extraction with dichloromethane, the organic extracts were washed with saturated aqueous sodium hydrogen carbonate and then with water. The organic phase was dried over anhydrous sodium sulfate and the solvent evaporated. The residue was chromatographed on silica gel using ethyl acetate/ethanol (9:1) as eluent to afford the compound: yield, 716 mg, 49%; mp 79−80 °C; ^{1}H NMR [$(CD_3)_2SO$] δ 3.36 (s, 2H), 3.63 (s, 3H), 3.75 (s, 2H), 6.70−6.75 (m, 2H), 7.04−7.10 (m, 2H). Anal. Calcd(Found): C, 61.8(61.5); H, 6.8(6.7); N, 7.0(7.2).

Complex Preparations. As the general procedure for preparing binary complexes was the same, the first example given is generally applicable with procedures different from those listed subsequently. Yields ranged from 44 to 70%.

[Cu(HSGly)$_2$]·0.5H_2O (1). Addition of a solution of H_2SGly (181 mg, 1.00 mmol) and LiOH (24 mg, 1.00 mmol) in water (20 cm^3) to copper(II) acetate monohydrate (100 mg, 0.50 mmol) in ethanol (10 cm^3) gave a light green product. This was filtered off and washed with water, ethanol, and diethyl ether before drying *in vacuo*. Yield: 134 mg, 74%.

[{Cu(SGly)}$_2$]·2H_2O (2). Copper(II) acetate monohydrate (430 mg, 2.00 mmol) in ethanol (15 cm^3) was added to a previously filtered solution of H_2SGly (181 mg, 1.00 mmol) in hot water (20 cm^3). The precipitate was filtered off and washed several times with water, ethanol, and then diethyl ether before drying *in vacuo*. Yield: 106 mg, 46%.

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[Cu(SAla)phen]·H_2O (5) and [Cu(SAla)Him] (7). To the royal blue solution formed from copper(II) acetate monohydrate (200 mg, 1.00 mmol) in ethanol (15 cm^3) and imidazole (146 mg, 2 mmol) or 1,10-phenanthroline (180 mg, 1.00 mmol) in ethanol (10 cm^3) was added a filtered solution of H_2SAla (200 mg, 1.00 mmol) in water (20 cm^3) with KOH (1.0 cm^3, 1 M). The dark green solutions were stirred for 2 h and then filtered and left for several days, after which time crystalline solids had formed that were filtered off, washed with ethanol, and dried *in vacuo*. Yields: **5**, 259 mg, 57.0%; **7**, 177 mg, 53.8%.

[Cu(SAla)py]·H_2O (6). Upon gentle heating of $[Cu(HSAla)_2]$ (487 mg, 1.00 mmol) in excess pyridine (10 cm^3) the complex dissolved. The filtered solution was left to evaporate at room temperature and after 2 weeks dark green crystals were collected and dried *in vacuo*. Yield: 237 mg, 67%.

[{Cu(SIle)}$_2$] (9). To a filtered solution of H_2SIle (245 mg, 1.03 mmol) and LiOH (25 mg, 1.05 mmol) in hot water (25 cm^3) was added copper(II) acetate monohydrate (200 mg, 1.00 mmol) in ethanol (10 cm^3). The resulting light green powder was filtered off and washed with water before drying *in vacuo*. Complexes **11** and **13** were prepared similarly. Yields ranged from 48 to 80%.

[Cu(SGlyMe)$_2$] (14). To a solution of HSGlyMe (310 mg, 1.50 mmol) in methanol (15 cm^3) was added a solution of copper(II) acetate monohydrate (157 mg, 0.75 mmol) in methanol (5 cm^3). The mixture was stirred for 1 h. The dirty green precipitate was filtered off and washed with methanol prior to drying *in vacuo*. Yield: 300 mg, 66.4%.

Materials. Reagents were purchased from the following suppliers: amino acids, Sigma; salicylaldehyde, copper(II) acetate, glycine methyl ester hydrochloride, imidazole, and 2,2′-bipyridyl, Fluka; 1,10-phenanthroline monohydrate, Aldrich. Solvents were purified by standard procedures.

X-ray Crystallography. 1. [Cu(SAla)phen]·H_2O. (a) Crystal Data. $C_{22}H_{21}CuN_3O_4$: triclinic, space group $P\bar{1}$; $a = 8.718(2)$ Å, $b = 10.886(3)$ Å, $c = 11.693(2)$ Å, $\alpha = 71.32(2)°$, $\beta = 85.27(2)°$, $\gamma = 70.21(2)°$; $V = 988.8(4)$ Å^3, $Z = 2$; $M = 455.0$ g mol^{-1}; $D_c = 1.582$ g cm^{-3}; absorption coefficient 1.140 mm^{-1}; $\lambda = 0.710\ 73$ Å; $F(000) = 470$; crystal dimensions $0.35 \times 0.20 \times 0.20$ mm.

(b) Measurements. Refined unit-cell parameters were found by centering 19 reflections, in the range $20° < 2\phi < 40°$, on a Siemens R3m/V diffractometer. A total of 3753 data points was measured, of which 3499 were unique, in the range $3.5 \le 2\phi \le 50.0°$ with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and index ranges $0 \le h \le 10$, $-12 \le k \le 12$, and $-13 \le l \le 13$ with a variable scan rate of 3.00−29.30° min^{-1}. Of these, 3091 reflections had $F > 4.0\ \sigma(F)$ and were considered to be observed for the purposes of structure solution and refinement. Two standard reflections were monitored every 98 reflections and showed no significant loss during data collection. The data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction by psi scan was applied.

(c) Structural Analysis. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to Ow were located from difference maps. The other hydrogen atoms were put at calculated positions with a fixed distance (0.960 Å) from carbon atoms and were assigned fixed thermal parameters. A total of 272 parameters was refined. The function minimized during full-matrix least-squares refinement was $\sum w|F_o - F_c|^2$ where $w^{-1} = \sigma^2(F) + 0.0029F^2$, giving $R = 0.0317$ and $R_w = 0.0537$. The final Fourier difference map was featureless, with a largest peak of 0.33 e Å^{-3}. Positional parameters are listed in Table 2. All calculations were performed using the Siemens SHELXTL PLUS-PC program package.

2. [Cu(SAla)Him]. (a) Crystal Data. $C_{13}H_{15}CuN_3O_3$: monoclinic, space group $P2_1/n$; $a = 10.353(1)$ Å, $b = 6.714(1)$ Å, $c = 18.769(2)$ Å, $\beta = 91.71(1)°$, $V = 1304.1(3)$ Å^3, $Z = 4$; $M = 324.8$ g mol^{-1}; $D_c = 1.654$ g cm^{-3}; absorption coefficient 1.686 mm^{-1}; $\lambda = 0.710\ 73$ Å; $F(000) = 668$; crystal dimensions $0.40 \times 0.36 \times 0.16$ mm; temperature of measurement = 188(2) K.

(b) Measurements. Intensity data were collected for a dark blue, block-shaped crystal at 188 K on a Siemens P4 diffractometer. Final lattice parameters were determined by least-squares treatment, using the setting angles of 27 well-centered reflections in the range $10.3 \le 2\theta \le 24.9°$. The unit cell parameters were checked for the presence of higher lattice symmetry. Data were collected in ω-scan mode. From a total of 4811 reflections in the range $2 \le \theta \le 22.5°$ (1710 unique), 4402 satisfied the $I > 2(I)$ criterion of observability. Data were corrected for Lorentz and polarization effects and for a decay of 4.3% of the three periodically measured reference reflections (3 1 0, 1 4 1, 6 1 −2), and a face-indexed absorption correction was applied (range of transmission coefficients 0.572−0.769).

(c) Structural Analysis. The structure was solved by automated direct methods (SHELXS90).[21] Refinement, based on F*2*, was carried out by full-matrix least-squares techniques (SHELXL93).[22] Hydrogen atoms were included in the refinement in calculated positions, riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters; the hydrogen thermal displacement parameters were fixed at 1.2 and 1.5 times the equivalent isotropic thermal displacement parameters of their internal and terminal carrier atoms, respectively. Convergence was reached at $R_F = 0.0348$ [for 4402 reflections with $I > 2\sigma(I)$], $R_wF2 = 0.0922$ (for all data), and $S = 1.132$ based on F_o^2, for 183 parameters. A final difference Fourier map showed no residual electron density outside −0.706 and 0.905 (near Cu) e Å^{-3}. Positional parameters are listed in Table 3. Neutral atom scattering factors and absorption coefficients were taken from *International Tables for Crystallography, Volume C*, 1992.

Physical Measurement. The electronic transmittance spectra were recorded on a Shimadzu UV-1601 UV−vis spectrophotometer using Nujol mulls and in DMSO solution. Microanalyses (Table 1) were performed by the microanalysis unit at the National University of Singapore. Room-temperature magnetic susceptibility measurements were carried out at on a Johnson−Matthey Magnetic Susceptibility balance with $Hg[Co(SCN)_4]$ as standard. Corrections for diamagnetism were made using Pascal's constants.[23] Conductance measurements were made using a Kyoto Electronics CM-115 conductivity meter with a Kyoto Electronics conductivity cell on ca. 1 mM solutions. The ^{1}H NMR spectra were recorded on a Bruker ACF 300 spectrometer operating in the quadrature mode at 300 MHz for solutions in DMSO-d_6 with $SiMe_4$ as internal standard. Infrared spectra were recorded on a Shimadzu IR-470 infrared spectrophotometer as KBr disks in the range 4000−400 cm^{-1}.

Molecular Mechanics Calculations. Molecular modeling, visualization and analysis were performed using SYBIL[24] running on a Silicon Graphics Onyx computer. The Tripos force field (6.0),[24] including the expanded metal parameter set (metal.tpd), was employed with the following modifications to the default parameter set for **7**. To reproduce the experimental square planar Cu(II), angles about Cu were set to 90° and 180° with the default force constant of 0.02 kcal mol^{-1} deg^{-2}, the out-of-plane bend was set to 230 kcal mol^{-1} deg^{-2} and the following torsions were defined: C11−N2−Cu−O12, 1.33°, 600 kcal mol^{-1} deg^{-2}; N2−Cu−O12−C1, 180°, 0.80 kcal mol^{-1} deg^{-2}; Cu−O12−C1−O11, 180°, 0.004 kcal mol^{-1} deg^{-2}; N2−Cu−O6−C6, 180°, 0.004 kcal mol^{-1} deg^{-2}. The Cu−N distances from the crystal structure were employed with an average Cu−O distance of 1.94 Å together with a Cu−ligand force constant of 600 kcal mol^{-1} Å^{-2}. The imidazole was treated as an aggregate. For **5**, the complex was treated as an octahedron with a lone pair, with Cu bond distances as in the X-ray structure and a force constant of 600 kcal mol^{-1} Å^{-2}. Angles about the Cu ion were as observed in the X-ray structure with a force constant of 0.04 kcal mol^{-1} deg^{-2}, except for the phen bite angle which was set at 400 kcal mol^{-1} deg^{-2}. The following torsions were set, by using the observed bond angles unless indicated otherwise, to best reproduce the X-ray structure observed: O6−Cu−N2−C20, 400 kcal mol^{-1} deg^{-2}; O6−Cu−N3−C21, 400 kcal mol^{-1} deg^{-2}. N3−Cu−N1−C4, 0.2 kcal mol^{-1} deg^{-2}; Cu−O12−C1−O11, 180°, 0.004 kcal mol^{-1} deg^{-2}; N2−Cu−O12−C1, 180°, 0.002 kcal mol^{-1} deg^{-2}; N2−Cu−O6−C6, 155.0°, 0.002 kcal mol^{-1} deg^{-2}.

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Table 1. Elemental Analysis, Colors, and Effective Magnetic Moments of Complexes

	complex	color	analysis (%)[a] C	H	N	μ_{eff}[b]/μ_B
1	$[Cu(HSGly)_2]\cdot 0.5H_2O$	light green	50.2(49.9)	4.9(4.9)	6.5(6.5)	2.23
2	$[\{Cu(SGly)\}_2]\cdot 2H_2O$	green	41.3(41.5)	4.0(4.3)	5.4(5.4)	1.55
3	$[Cu(HSAla)_2]\cdot 2H_2O$	light blue	53.1(53.1)	4.9(5.3)	6.0(6.2)	1.95
4	$[\{Cu(SAla)\}_2]\cdot 2H_2O$	green	40.6(41.0)	4.7(5.1)	4.8(4.8)	1.31
5	$[Cu(SAla)phen]\cdot H_2O$	dark green	58.0(58.0)	4.5(4.6)	9.0(9.2)	1.79
6	$[Cu(SAla)py]\cdot H_2O$	green	50.9(50.9)	5.2(5.1)	8.0(7.9)	1.83
7	[Cu(SAla)Him]	dark green	47.4(48.0)	4.7(4.7)	12.9(12.9)	1.79
8	$[Cu(HSIle)_2]\cdot 2.5H_2O$	green	54.0(53.8)	5.7(5.7)	4.8(4.8)	2.07
9	$[\{Cu(SIle)\}_2]$	light green	52.0(52.3)	5.7(5.7)	4.7(4.7)	1.84
10	$[Cu(HSLeu)_2]\cdot H_2O$	green	56.3(56.4)	6.4(6.9)	5.0(5.1)	2.24
11	$[\{Cu(SLeu)\}_2]\cdot H_2O$	turquoise	48.2(47.9)	5.5(6.2)	4.2(4.3)	1.57
12	$[Cu(HSPhe)_2]\cdot 3H_2O$	green	58.5(58.4)	5.4(5.8)	4.3(4.2)	1.99
13	$[\{Cu(SPhe)\}_2]$	blue	57.7(57.7)	4.8(4.5)	4.2(4.2)	1.78
14	$[Cu(SGlyMe)_2]$	green brown	53.1(53.1)	4.9(5.3)	6.0(6.2)	1.87

[a] Calculated values are given in parentheses. [b] At 293 K per metal ion.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Cu(SAla)phen]\cdot H_2O$ (**5**) with Estimated Standard Deviations in Parentheses

	x	*y*	*z*	*U*(eq)
Cu	725(1)	2125(1)	2234(1)	31(1)
C(1)	−1397(3)	1112(3)	3833(2)	38(1)
C(2)	−1296(3)	2319(3)	4202(2)	38(1)
C(3)	−1710(4)	2218(3)	5501(3)	52(1)
C(4)	472(3)	3762(3)	3874(2)	38(1)
C(5)	2049(3)	3976(3)	3365(2)	35(1)
C(6)	2445(3)	3954(2)	2174(2)	33(1)
C(7)	3835(3)	4260(3)	1679(3)	40(1)
C(8)	4788(4)	4629(3)	2335(3)	51(1)
C(9)	4398(4)	4632(3)	3501(3)	53(1)
C(10)	3035(4)	4306(3)	4005(3)	44(1)
C(11)	4324(3)	−247(3)	3160(3)	46(1)
C(12)	5596(4)	−1405(3)	3091(3)	55(1)
C(13)	5621(4)	−1921(3)	2175(3)	52(1)
C(14)	4384(3)	−1241(3)	1268(3)	40(1)
C(15)	4354(4)	−1653(3)	222(3)	50(1)
C(16)	3198(4)	−922(3)	−649(3)	47(1)
C(17)	1928(3)	291(3)	−559(2)	37(1)
C(18)	718(4)	1110(3)	−1467(2)	45(1)
C(19)	−454(4)	2251(3)	−1313(2)	42(1)
C(20)	−430(3)	2564(3)	−251(2)	38(1)
C(21)	1891(3)	695(2)	466(2)	30(1)
C(22)	3149(3)	-64(3)	1398(2)	33(1)
N(1)	354(3)	2433(2)	3851(2)	32(1)
N(3)	3097(3)	411(2)	2333(2)	36(1)
N(2)	701(3)	1824(2)	617(2)	31(1)
O(11)	−2131(3)	352(2)	4431(2)	50(1)
O(12)	−685(3)	1013(2)	2842(2)	44(1)
O(6)	1489(2)	3684(2)	1513(2)	36(1)
Ow	1829(3)	4584(2)	8996(2)	53(1)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for [Cu(SAla)Him] (**7**) with Estimated Standard Deviations in Parentheses

	x	*y*	*z*	*U*(eq)
Cu	1442(1)	1272(1)	3186(1)	14(1)
O(6)	3071(2)	1750(4)	2751(1)	16(1)
O(12)	−244(2)	721(4)	3584(1)	18(1)
O(11)	−2195(2)	−451(4)	3286(3)	21(1)
N(1)	550(3)	711(5)	2262(2)	14(1)
N(3)	2477(3)	1250(5)	5295(2)	18(1)
N(2)	2235(3)	1499(5)	4136(2)	14(1)
C(1)	−1142(4)	252(6)	3129(2)	16(1)
C(2)	−876(3)	722(6)	2355(2)	17(1)
C(3)	−1600(4)	−585(7)	1823(2)	24(1)
C(4)	974(3)	2081(6)	1700(2)	18(1)
C(5)	2340(4)	1689(5)	1518(2)	15(1)
C(6)	3299(4)	1471(5)	2061(2)	14(1)
C(7)	4552(4)	1000(6)	1860(2)	16(1)
C(8)	4859(4)	856(6)	1153(2)	18(1)
C(9)	3938(4)	1162(6)	622(2)	19(1)
C(10)	2678(4)	1525(6)	812(2)	17(1)
C(11)	1647(4)	1256(5)	4741(2)	16(1)
C(12)	3678(4)	1497(6)	5031(2)	21(1)
C(13)	3536(3)	1653(6)	4320(2)	18(1)

Results and Discussion

To overcome the general problems of ligand instability for Schiff bases of amino acids, and to introduce greater ligand flexibility and model the proton-shifted intermediate of transamination reactions, an *in situ* reduction was carried out on the salicylaldehyde−amino acid mixture. The conditions employed gave satisfactory elemental analyses for the ligands; however, they were isolated as racemates. This was unexpected as the conditions employed were similar to those previously used to isolate optically active material, namely, the reaction temperature was kept to 30 °C with a reaction time of 30 min. Optically active Schiff bases between, for example, salicylaldehyde or pyridoxal and Ala, Val, Phe, and His have been reported[25] by refluxing the reagents for 2 h, and H_2Sal-L-His was prepared by a procedure analogous to ours.[18,26] A survey of such ligand preparations does not show any apparent pattern to when racemization occurs, although the presence of a metal may favor the retention of chirality by acting as a template.

Addition of copper(II) salt to ligand in aqueous solution led to the precipitation of the binary complexes. The ternary adducts $[Cu(SAla)phen]\cdot H_2O$ (**5**) and [Cu(SAla)Him] (**7**) were prepared by adding the nitrogen base, either phen or Him, to the copper salt followed by addition of the H_2SAla ligand. Alteration of the order of addition of reagents had no effect on the product. However, when $[Cu(HSAla)_2]\cdot 2H_2O$ (**3**) is treated with excess pyridine, the ternary adduct $[Cu(SAla)py]\cdot H_2O$ (**6**) in which one ligand has been displaced and the remaining deprotonated was isolated. All complexes are stable at room temperature. Microanalytical data are listed in Table 1 together with complex colors and magnetic moments. The presence of hydrated water was confirmed by a broad absorption at ca. 3450 cm^{-1} in infrared spectra for the ligands and complexes. However, the spectra were complicated with numerous bands, and assignments based on these therefore were not undertaken.

Crystal Structure of $[Cu(SAla)phen]\cdot H_2O$ (5). A thermal ellipsoid diagram giving the unique atom labeling is shown in Figure 1. Selected bond distance and angle data are given in

(25) Casella, L.; Guillotti, M. *Inorg. Chem.* **1986**, *25*, 1293−1303.

(26) (a) Meiske, L. A.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1980**, *19*, 2028−2034. (b) Meiske, L. A.; Angelici, R. J. *Inorg. Chem.* **1980**, *19*, 3783−3789.

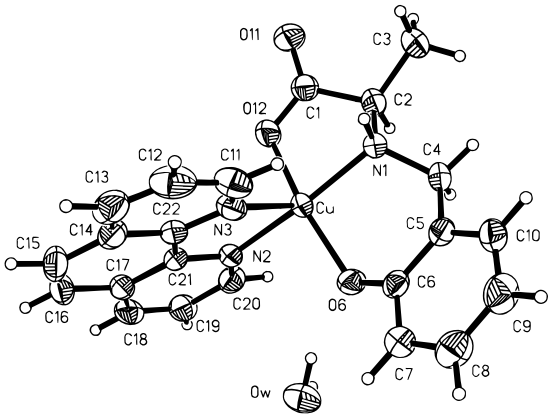

Figure 1. Structure of [Cu(SAla)phen]·H_2O (**5**) showing the numbering scheme (hydrogen atoms are not labeled for clarity).

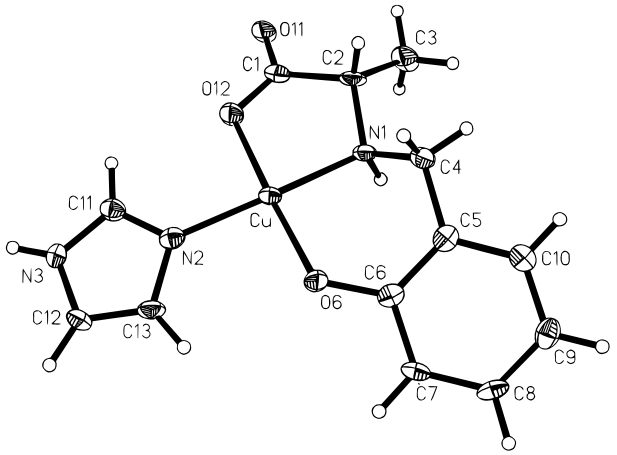

Figure 2. Structure of [Cu(SAla)Him] (**7**) showing the numbering scheme (hydrogen atoms are not labeled for clarity).

Tables 4 and 5, respectively. The structure consists of monomeric units with the copper center as an approximate square pyramidal geometry. The four basal positions are occupied by the tridentate, dianionic SAla ligand, which furnishes an ONO donor set, with the fourth position occupied by a phen N. The coordination sphere is completed by the remaining phen N binding at the apex. The phen is planar and lies at an angle of 84° to the plane of best fit through the tridentate SAla ligand.

To our knowledge, this is the first structure of this ligand. In addition, it is the only one of copper with a reduced chiral amino acid Schiff base. The only others for this general class of ligand are Co(III) in [α-*N*-(*o*-hydroxybenzyl)-L-histidinato]-(L-alaninato)cobalt(III) dihydrate[18] ([Co(SalHis)Ala]·$2H_2O$) and the complexes of (*o*-hydroxybenzyl)glycinate (H_2SGly)[19] ([{Cu-(SGly)}$_2$(H_2O)]·H_2O and [$Co(NH_3)_6$][$Co(SGly)_2]_2Cl$). The in-plane distances for **5** therefore will be compared with those of [{Cu(SGly)}$_2$(H_2O)]·H_2O and the averages of those for Cu(II) with amino acid−salicylidene complexes.[15] The Cu−amine distance [Cu−N(1), 2.007(2) Å] in **5** is significantly longer than the Cu−imine length observed [1.939(15) Å]. The bond to the phenolato O [Cu−O(6), 1.947(2) Å] is also longer (1.912 Å). The decrease in conjugation upon reducing the imine will result in reduced charge delocalization, which is seen in the longer bond distances. The distance to the carboxylato O [Cu−O(12), 1.948(2) Å] is not significantly different from that in the imine structures (1.956 Å). The remaining in-plane site is to the phen [Cu−N(2), 2.022(2) Å]. The best-fit least-squares plane through the four basal and Cu atoms shows a small tetrahedral distortion with an average distance from the plane of 0.104 Å. The Cu atom lies 0.167 Å out of the plane toward the apex of the pyramid, as is seen in salicylidene−amino acid structures.[11ab,15i,27] The final bond to the Cu atom, completing the coordination sphere, is to the remaining phen nitrogen [Cu−N(3), 2.249(2) Å] in an axial position, with this increase in distance being typical for Jahn−Teller-distorted Cu(II).[27]

The successful *in situ* reduction of the imine is evident from the N(1)−C(4) distance [1.493(4) Å] when compared with the average distance seen for related salicylidene ligands with Cu(II) (1.27−1.30 Å). Further, the distances for C(4)−C(5) [1.514(4) Å] and N(1)−C(2) [1.498(4) Å] are typical of single bonds, being significantly longer than those of imine complexes[15] and indicating the loss of conjugation. The angles centered about N(1) are consistent with an sp^3 tetrahedral N and are similar to those for Co(SalHis)Ala.[18] The exception is C(4)−N(1)−C(2), which is 112.0(2)° for **5** but 117.3(5)° for Co(SalHis)Ala. This is probably due to the histidine imidazole coordination in the latter structure, giving a tetradentate ligand and forcing the angular changes about the chiral center C(2). The observed difference between the coordinated and uncoordinated carboxylate oxygens is typical for such structures.[15a,c−g,18]

In addition to the asymmetric center in the ligand at atom C(2) (*R* as shown in Figure 1), the coordination of the SAla ligand to the metal ion gives rise to an asymmetric secondary nitrogen atom N(1), which has the *S* absolute configuration in Figure 1. The observed trans configuration should result in less steric interactions. The $P\bar{1}$ space group means that the other molecule in the unit cell, related by an inversion center, has opposite chirality for both C(2) and N(1) and the two molecules therefore are diastereoisomers.

Intermolecular hydrogen bonds through the waters of crystallization occur in the crystal. The water oxygen atom (Ow) is within hydrogen-bonding distance (2.813 Å) of the phenolate oxygen O_6 and is 2.855 Å from O_6 in symmetry-related molecules. One other apparent hydrogen-bonding interaction involves direct interaction of the alaninate carboxyl oxygen O_{11} with nitrogen N_1 of an adjacent molecule (3.01 Å).

Crystal Structure of [Cu(SAla)Him] (7). A thermal ellipsoid diagram giving the unique atom labeling is shown in Figure 2. Selected bond distance and angle data are given in Tables 4 and 5, respectively. The structure consists of monomeric units with the copper center in a square planar geometry. The four positions are occupied by the tridentate, dianionic SAla ligand with the final position taken by an imidazole N. The closest axial approaches to the Cu are at ca. 3.3 Å to C(6) and C(7) from symmetry-related molecules.

The average in-plane bonding distance in **7** is significantly shorter than that for **5**, with the stronger bonding compensating for the lower coordination number in **7**. The best-fit least-squares plane through the four basal and Cu atoms shows these atoms to be nearly coplanar. The O(12)−Cu−O(6) angle of 177.09(9)° is nearly linear and considerably greater than the 162.4(1)° seen in **5**, where steric constraints of the chelated phen and the adoption of a square pyramidal geometry have forced the oxygen donors out of the plane. Effects of this are seen for Cu−O(6)−C(6), where the angle has opened up by 5.6° in **7**, and around the chiral N(1), where the Cu−N(1)−C(4) angle has decreased by 3.2° and Cu−N(1)−C(2) has increased 4.5° relative to **5**. Bond lengths within the dianionic SAla ligand in

(27) (a) Clifford, F.; Counihan, E.; Fitzgerald, W.; Seff, K.; Simmons, C.; Tyagi, S.; Hathaway, B. *J. Chem. Soc., Chem. Commun.* **1982**, 196−201. (b) Castro, R.; Durán, M. L.; Garcia-Vázquez, J. A.; Romero, J.; Sousa, A.; Castiñeiras, A.; Hiller W.; Strähle, J. *Polyhedron* **1992**, *11*, 1195−1200. (c) Anderson, O. P. *J. Chem. Soc., Dalton Trans.* **1973**, 1237−1241. (d) Rajender-Reddy, K.; Rajasekharan, M. V. *Polyhedron* **1994**, *13*, 765−769.

Table 4. Selected Bond Lengths (Å) for [Cu(SAla)phen]·H_2O (**5**) and [Cu(SAla)Him] (**7**) with Estimated Standard Deviations in Parentheses

	5		**7**
Cu−N(1)	2.007(2)		1.976(3)
Cu−N(3)	2.249(2)		
Cu−N(2)	2.022(2)		1.947(3)
Cu−O(12)	1.948(2)		1.954(2)
Cu−O(6)	1.947(2)		1.923(2)
C(1)−C(2)	1.539(5)		1.521(5)
C(1)−O(11)	1.223(4)		1.232(4)
C(1)−O(12)	1.286(3)		1.282(4)
C(2)−C(3)	1.511(4)		1.511(5)
C(2)−N(1)	1.498(4)		1.492(5)
C(4)−C(5)	1.514(4)		1.488(5)
C(4)−N(1)	1.493(4)		1.477(5)
C(5)−C(6)	1.412(4)		1.410(5)
C(5)−C(10)	1.385(5)		1.384(5)
C(6)−C(7)	1.396(4)		1.398(5)
C(6)−O(6)	1.340(4)		1.336(4)
C(7)−C(8)	1.404(5)		1.377(5)
C(8)−C(9)	1.379(5)		1.374(5)
C(9)−C(10)	1.385(5)		1.385(6)
		N(2)−C(11)	1.314(5)
		N(2)−C(13)	1.384(5)
		N(3)−C(11)	1.328(5)
		N(3)−C(12)	1.362(5)
		C(12)−C(13)	1.341(5)

7 are similar to those for **5** with a number of minor differences in bond angles (*vide supra*).

The asymmetric C(2) and N(1) centers have the *S* and *R* absolute configurations, respectively, as depicted in Figure 2. The presence of a crystallographic mirror plane means that symmetry-related molecules have these centers with opposite chirality, and as for **5**, the molecules in the solid state are diastereoisomers with a trans configuration about C(2)−N(1).

The imidazole is planar and lies at an angle of 10° to the plane of best fit through the copper coordination sphere. This is similar to the arrangement found for the coordinated pyrazole in [Cu(salicylidene-*S*-alaninato)pyrazole]·pyrazole.[15i] Bond distances and angles within the Him moiety are normal.[28] A hydrogen bond between the Him N(3) and O(11) (2.74 Å) helps to hold molecules in pairs in the *a*−*c* plane, with a weak contact between the amino acid N(1) and the coordinated phenolato O(6) (3.02 Å) stacking them in *b*.

Physicochemical Studies. Electronic spectral data for the complexes as Nujol mulls are presented in Table 6. The mull transmittance spectra exhibit a charge transfer transition (ct) at ca. 400 nm, which may be assigned to a ligand to copper(II) transition. The exceptions to this are **1** and **3**, which contain monodeprotonated ligands and are assumed to have only the carboxylate deprotonated. The ct transition therefore is assigned as phenolato to copper, and the absence of this absorption may tentatively be used as an indication of the coordination mode for these ligands. Credence is given to this as in **14** where the monodeprotonated ligand has the carboxylate esterified. The ct band is seen at 410 nm showing phenolato coordination. Schiff base complexes of salicylaldehyde with Gly and acetyllysine[9] and Ala, Val, Phe, and His[25] exhibit this band at higher energy, ca. 360 nm. The delocalization of charge in the conjugated Schiff base ligands would be expected to shift the ct band to higher energy, as is seen. Cu(SalGly) (where SalGly is salicylaldimine glycinate) and related systems also display a ct band at ca. 265 nm assigned as a $\pi^* \leftarrow \pi$ transition, which was considered indicative of the salicylaldimine group moiety in a dianionic ligand. The shift in the ct band to lower energy at 280−295 nm (DMSO) for this work, where the imine has been reduced, reinforces this assignment.

Complexes **1** and **3**, which have a 1:2 Cu:ligand ratio and a d−d band at 600 nm, are assigned square planar geometries

Table 5. Selected Bond Angles (deg) for [Cu(SAla)phen]·H_2O (**5**) and [Cu(SAla)Him] (**7**) with Estimated Standard Deviations in Parentheses

	5		**7**
N(1)−Cu−N(3)	108.5(1)		
N(1)−Cu−N(2)	170.3(1)		172.67(13)
N(3)−Cu−N(2)	78.2(1)		
N(1)−Cu−O(12)	83.2(1)		84.23(11)
N(3)−Cu−O(12)	98.3(1)		
N(2)−Cu−O(12)	89.0(1)		91.27(11)
N(1)−Cu−O(6)	94.2(1)		92.98(11)
N(3)−Cu−O(6)	99.0(1)		
N(2)−Cu−O(6)	91.5(1)		91.42(11)
O(12)−Cu−O(6)	162.4(1)		177.09(9)
C(2)−C(1)−O(11)	121.7(3)		119.7(3)
C(2)−C(1)−O(12)	113.8(3)		115.9(3)
O(11)−C(1)−O(12)	124.4(3)		124.4(3)
C(1)−C(2)−C(3)	113.8(3)		114.2(3)
C(1)−C(2)−N(1)	106.4(2)		108.5(3)
C(3)−C(2)−N(1)	115.0(3)		113.2(3)
C(5)−C(4)−N(1)	112.6(2)		111.0(3)
C(4)−C(5)−C(6)	119.1(3)		120.4(3)
C(4)−C(5)−C(10)	121.2(3)		120.2(3)
C(6)−C(5)−C(10)	119.5(3)		119.4(3)
C(5)−C(6)−C(7)	118.7(3)		117.9(3)
C(5)−C(6)−O(6)	121.2(2)		123.1(3)
C(7)−C(6)−O(6)	120.1(2)		119.0(3)
C(6)−C(7)−C(8)	120.7(3)		121.2(3)
C(7)−C(8)−C(9)	120.0(3)		120.9(3)
C(8)−C(9)−C(10)	119.6(4)		118.5(3)
C(5)−C(10)−C(9)	121.5(3)		121.9(4)
Cu−N(1)−C(2)	105.1(2)		109.6(2)
Cu−N(1)−C(4)	114.7(2)		111.5(2)
C(2)−N(1)−C(4)	112.0(2)		113.3(3)
Cu−N(3)−C(11)	132.9(2)		
Cu−N(3)−C(22)	109.1(1)		
C(11)−N(3)−C(22)	117.7(2)	C(11)−N(3)−C(12)	106.9(3)
Cu−N(2)−C(20)	125.4(2)	C(11)−N(2)−Cu	126.0(3)
Cu−N(2)−C(21)	116.0(2)	C(13)−N(2)−Cu	127.9(2)
C(20)−N(2)−C(21)	118.3(2)	C(11)−N(2)−C(13)	105.4(3)
Cu−O(12)−C(1)	115.8(2)		115.5(2)
Cu−O(6)−C(6)	119.2(1)		124.8(2)
		N(2)−C(11)−N(3)	111.8(3)
		N(3)−C(12)−C(13)	107.3(3)
		N(2)−C(13)−C(12)	108.6(3)

Table 6. Electronic Absorption and Conductivity Data for Complexes

	complex	absorption bands (nm)[a] charge transfer	d−d	molar conductivity[b]
1	[Cu(HSGly)$_2$]·0.5H_2O	sh	600	0
2	[{Cu(SGly)}$_2$]·2H_2O	386	670	0
3	[Cu(HSAla)$_2$]·2H_2O	sh	600br	4
4	[{Cu(SAla)}$_2$]·2H_2O	390sh	685	2
5	[Cu(SAla)phen]·H_2O	400	720	1
6	[Cu(SAla)py]·H_2O	386	660br	0
7	[Cu(SAla)Him]	395	620	1
8	[Cu(HSIle)$_2$]·2.5H_2O	sh	690	2
9	[{Cu(SIle)}$_2$]	400sh	725	1
10	[Cu(HSLeu)$_2$]·H_2O	sh	700br	1
11	[{Cu(SLeu)}$_2$]·H_2O	400sh	680	0
12	[Cu(HSPhe)$_2$]·3H_2O	sh	740br	3
13	[{Cu(SPhe)}$_2$]	400sh	660br	0
14	[Cu(SGlyMe)$_2$]	410	600	1

[a] Nujol mull transmittance spectra. [b] In $(CH_3)_2SO$, S cm^{-2} mol^{-1}.

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on the basis of a comparison with the square planar **7**, which exhibits a d−d transition at 620 nm. The monodeprotonated HSGly and HSAla ligands therefore are acting as bidentate chelators, coordinating through the carboxylato O and amino N. This is in contrast to amino acid−salicylidene complexes studied by single-crystal X-ray diffraction where ligands invariably were shown to coordinate as tridentate moieties, incorporating the phenolato O. The square pyramidal Cu(II) in **5** has its ligand field transition at longer wavelength, consistent with the change in geometry.[29] In $(CH_3)_2SO$ solution the d−d transition does not shift significantly (data not shown), except for **9** where the band moves from 725 to 660 nm, indicating a structural change from a square pyramidal 4+1 geometry in the solid to a solvated 4+2 tetragonal structure in solution. Molar conductance values in $(CH_3)_2SO$ indicate that all complexes are nonelectrolytes, showing that the ligand remains bound, without further deprotonation, even in such a strongly coordinating solvent.

The depressed room-temperature magnetic moments for **2** (1.55 μ_B), **4** (1.31 μ_B), and **11** (1.57 μ_B) indicate moderately strong antiferromagnetic coupling for these complexes. The structures for these species and those of the other binary dianionic ligands (**9**, **11**, and **13**) are assigned as side-by-side dimers and assumed to have bridging phenolato moieties. Dimers bridged through the carboxylate have been considered by several authors, but in light of the X-ray structures of Cu(II) with the tyrosine analog[30] of the present system, $[\{Cu(STyr)\}_2]\cdot 3H_2O$, and structurally related salicylaldehyde acylhydrazones,[31] we consider this less probable. The related Schiff base complexes $\{Cu(SalVal)\}_2$ and $\{Cu(SalLeu)\}_2$ were also proposed to be dimers due to their low magnetic moments of 1.35 and 1.56 μ_B, respectively,[2] and Gly analogs of these, $[\{Cu(SalGly)\}_2]\cdot nH_2O$, were found to have moments between 1.33 and 1.86 μ_B, depending on the state of hydration and crystallinity.[32] Interestingly, the crystal structure of the reduced-ligand complex $[\{Cu(SGly)\}_2(H_2O)]\cdot H_2O$ has been determined. In this the Cu(II) centers are bridged by the phenolato O, giving a planar Cu core with a metal−metal separation of 2.97 Å but a normal moment of 1.78 μ_B.[33] Our remaining complexes have μ_B values that are consistent with magnetically dilute copper(II) complexes, as evidenced for monomeric **5** and **7**, although the presence of weakly coupled dimers cannot be ruled out (*vide supra*).

Molecular Mechanics. Good agreement between the crystal and minimized structures was obtained by defining parameter sets for Cu in **5** and **7**. Torsions and angles around the metal were explored to give the best fit without unduly constraining the geometry. The observed *SR* and *RS* arrangements of the chiral C2 and N1 result in the two H-atoms being in axial positions about the five-membered chelate ring, while the methyl (C3) and methylene (C4, now in the six-membered chelate ring) take up equatorial positions. Inversion of either chiral center gives the diastereomers *SS* and *RR*, and minimization of this structure shows the effect of the steric interactions. For **7** the angle C2−N1−C4 increased by 2°, pushing C3 and C2 apart, accompanied by a significant flattening of the chelate rings as seen from the dihedral angle C1−C2−N1−C4, which increased from 146° for *SR* and *RS* to 158° for *SS* and *RR*. The effect of flattening the chelate rings has been to force the phenyl group down toward N1(H) by 8° compared to the observed structure. The net changes result in the *SS* and *RR* structures being more sterically strained and less likely to pack well in the solid state. In **5** the predominant changes upon inversion of C2 are seen in the carboxylate, where the torsion Cu−O12−C1−O11 decreases by 4.6° to 168.2°. The presence of the phen perpendicular to the SAla ligand appears to have decreased the magnitude of the effect when compared to **7** and may indicate less of an energy barrier to N1 inversion in this structure.

Our results agree with the proposed mechanism for amino acid racemization. The intermediate formed from protic solvent addition across the initially formed imine double bond gives a carbinolamine, where the sterically larger groups in the now saturated intermediate would occupy equatorial positions on the puckered chelate ring. Our crystal and energy-minimized structures agree with this prediction, and the complexes may serve as models for this imine-reduced intermediate.

Conclusions

Imine-reduced analogs of Schiff base ligands between amino acids with nonpolar side chains and salicylaldehyde binding copper(II) have yielded complexes with bi- or tridentate coordination modes, mono- and dideprotonated ligands, as well as binary and ternary adducts with Lewis bases. The complexes appear to the first of their kind containing derivatives of chiral amino acids with Cu(II) and may serve as models for the intermediate species in the biological racemization and transamination reactions of amino acids with pyridoxal phosphate. Adoption of a phenolato-bridged, dimeric structure for dianionic ligands is consistent with the resulting antiferromagnetic coupling between the Cu(II) centers observed in the majority of such complexes. The trans arrangement of the two chiral centers in the complexed ligand is considered to result from favorable steric interactions. Studies of amino acids possessing polar, and potentially coordinating, side chains are in progress to investigate their coordinating ability with Cu(II), especially that of histidine, for which the unstable Schiff base has been studied in detail but with no apparent crystallographic reports.

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Supporting Information Available: Tables detailing the X-ray data collection and refinement, atomic coordinates, bond distances, bond angles, anisotropic displacement coefficients, and H-atom coordinates for **5** and **7** (16 pages). Ordering information is given on any current masthead page.

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