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A Distorted Tetrahedral Copper(II) Complex of a Tetradentate Schiff Base Ligand

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The reaction of the ligand formed by the 2:1 molar condensation of salicylaldehyde with $\alpha,\alpha,\delta,\delta$-tetramethylputrescine with copper(II) results in the formation of the title compound, referred to hereafter as Cu(sal$_2$tmput). The crystal and molecular structure has been determined using single-crystal X-ray diffraction. The crystal is of the monoclinic class, space group *Cc*, with a = 14.374 (7) Å, b = 14.508 (3) Å, c = 19.370 (3) Å, β = 94.33 (8)°, and Z = 8. The asymmetric unit consists of two independent Cu(sal$_2$tmput) molecules having D_{2d}-distorted tetrahedral symmetry. The dihedral angles defined by the phenyl moieties bound to the copper atoms of the asymmetric pair are 52.4 and 45.6°, respectively. The distortion from the normal square-planar coordination markedly influences the chemical properties of the complex.

Introduction

Coordination complexes with substituted salicylaldehyde ligands have shown a diversity of structures and properties involving a number of stereochemistries and a wide range of bonding interactions.[2,3] Schiff base complexes are of particular interest to inorganic chemists because their structural, spectral, chemical, and electrochemical properties are often strongly dependent on the detailed ligand structure. Schiff base complexes of copper are specifically of interest in bioinorganic chemistry since these complexes provide inorganic models for copper proteins.[4,5]

The structure of Cu(sal$_2$tmput) has been determined as a part of a study of the effects of ligand structure on the chemical properties of Schiff base–metal complexes.[6,7] Of particular interest are comparisons of stereochemistry and electrochemical properties among Schiff base complexes of similar structure, e.g., bis(*N*-*tert*-butylsalicylaldiminato)copper(II), Cu(*t*-Bu-sal)$_2$,[8,9] (*N,N'*-ethylenebis(salicylideniminato)copper(II), Cu(sal$_2$en),[10] and Cu(sal$_2$tmput).

Experimental Section

General Data. Microanalyses were carried out by the Australian National University Microanalysis Service. Visible–near-infrared spectra were measured on a Cary 14 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. The spectra were run as Nujol mulls on KBr disks or as KBr pellets. Mass spectra were obtained on an AEI-MS9 instrument at both low and high resolution. Spectroelectrochemical studies were performed as previously described in the literature[7] (0.5 M Et$_4$NBF$_4$/DMF) vs. a standard calomel electrode. Common laboratory chemicals were of reagent grade.

2,5-Bis(salicylaldimino)-2,5-dimethylhexane (sal$_2$tmputH$_2$). Salicylaldehyde (24.42 g, 0.2 mol) was added directly to a solution of 2,5-dimethylhexane-2,5-diamine (tetramethylputrescine) (14.43 g, 0.1 mol) in 150 mL of absolute ethanol. The resulting reaction mixture was refluxed 1 h and allowed to cool. Bright yellow crystals were filtered off, washed twice with absolute methanol, and dried under vacuum (31.43 g, 89%). The product analyzed as $C_{22}H_{28}N_2O_2$. Calcd: C, 74.97; H, 8.01; N, 7.95. Found: C, 74.92; H, 7.76; N, 8.07. ν_{max} 1630, 1580, 1510, 1420, 1287, 1275, 1215, 1162, 1155, 1118, 1032, 980, 955, 943, 920, 885, 870, 800, 760, 745, 630, 568, 442 cm^{-1}. Mass spectrum 352 (60%), 218 (90%), 122 (100%). Mp 115.5–116.8 °C.

Cu(sal$_2$tmput). sal$_2$tmputH$_2$ (3.52 g, 0.01 mol) in 150 mL of absolute ethanol was added to a solution of copper(II) acetate (2.00 g, 0.01 mol) in 150 mL of absolute ethanol. A suspension of LiOH (0.84 g, 0.02 mol) in absolute ethanol was added and the reaction mixture heated to boiling and filtered.

The filtrate was evaporated and cooled to room temperature, yielding large brown crystals (3.67 g, 88%) which were washed with ethanol. The product was recrystallized from hot isopropyl alcohol and washed with heptane. Anal. Calcd for $CuC_{22}H_{26}N_2O_2$: Cu, 15.35; C, 63.82; H, 6.32; N, 6.77. Found: Cu, 15.50; C, 63.34; H, 6.41; N, 6.72. Mp 247–249 °C. ν_{max} 1610, 1540, 1472, 1450, 1405, 1358, 1335, 1195, 1180, 1150, 1130, 1120, 1030, 960, 865, 860, 800, 760, 745, 590, 510, 502, 450, 408 cm^{-1}. Mass spectrum 413 (parent ion), 352 (free ligand).

Crystals suitable for X-ray diffraction studies were grown by dissolving the recrystallized product in a minimal amount of isopropyl alcohol and layering an equal volume of *n*-heptane on the isopropyl alcohol solution. Solvent diffusion produced crystals of suitable quality in 2 to 3 days.

Spectroelectrochemistry. An optically transparent thin-layer electrode (OTTLE)[11] was employed in conjunction with cyclic voltammetry to electrochemically and spectrally characterize Cu(sal$_2$tmput). The compound is reduced by a negative scan initiated at −0.7 V. This couple is assigned as Cu(II) → Cu(I) with $E^{\circ\prime}$ = −0.722 V. vs. SCE, the $E^{\circ\prime}$ being determined[7] by a plot of $E_{applied}$ vs. log [O]/[R]. The system was shown to be reversible under the slow time scale of the OTTLE spectropotentiostatic experiment, where each potential is maintained until equilibrium is reached. Spectra of Cu(sal$_2$tmput) from spectropotentiometric experiments showed λ_{max} at 380 and 410 nm for the Cu(II) and Cu(I) species, respectively, with isosbestic points at 385 and 500 nm.

X-ray Characterization of Cu(sal$_2$tmput). A dark brown crystal of the Cu(sal$_2$tmput) complex was mounted on a glass fiber and precession photographs of the *hk*0, *hk*1, 0*kl*, and 1*kl* layers were taken using Cu Kα radiation. The systematic absences were for *hkl*, *h* + *k* odd, and for *h*0*l*, *l* odd, suggesting possible choices of space group[12]

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Table I. Fractional Atomic Positional Parameters^{a-c}

	x	y	z
Cu(1)	0.45478 (9)	0.21842 (7)	0.02008 (7)
Cu(2)	0.0 (0)	0.17582 (7)	0.0 (0)
O(1)	0.4342 (5)	0.0896 (4)	0.0233 (4)
O(11)	0.4242 (5)	0.2156 (5)	−0.0770 (4)
O(21)	0.0208 (4)	0.1647 (4)	0.0968 (3)
O(31)	−0.1285 (5)	0.1498 (5)	0.0102 (4)
N(9)	0.5605 (5)	0.2193 (5)	0.0918 (4)
N(19)	0.3955 (5)	0.3394 (4)	0.0352 (4)
N(29)	0.1215 (5)	0.1237 (5)	−0.0206 (4)
N(39)	−0.0269 (6)	0.2600 (5)	−0.0794 (4)
C(2)	0.5410 (8)	0.0583 (6)	0.1238 (6)
C(3)	0.5740 (8)	−0.0081 (8)	0.1731 (6)
C(4)	0.5326 (9)	−0.0979 (8)	0.1691 (6)
C(5)	0.4632 (9)	−0.1224 (8)	0.1197 (8)
C(6)	0.4301 (8)	−0.0594 (7)	0.0703 (6)
C(7)	0.4668 (7)	0.0329 (6)	0.0704 (5)
C(8)	0.5847 (7)	0.1483 (7)	0.1294 (5)
C(12)	0.3711 (6)	0.3724 (7)	−0.0883 (4)
C(13)	0.3374 (7)	0.4450 (7)	−0.1342 (5)
C(14)	0.3323 (9)	0.430 (1)	−0.2051 (6)
C(15)	0.3604 (8)	0.346 (1)	−0.2319 (6)
C(16)	0.3927 (7)	0.2748 (8)	−0.1886 (5)
C(17)	0.3964 (7)	0.2869 (8)	−0.1169 (5)
C(18)	0.1462 (6)	0.1059 (7)	−0.0950 (4)
C(41)	0.6165 (7)	0.3068 (6)	0.1050 (5)
C(42)	0.5660 (7)	0.3668 (7)	0.1564 (5)
C(43)	0.4806 (7)	0.4240 (6)	0.1317 (4)
C(44)	0.3890 (7)	0.3766 (6)	0.1093 (4)
C(45)	0.7184 (8)	0.2842 (9)	0.1375 (7)
C(46)	0.6282 (8)	0.3519 (6)	0.0337 (5)
C(47)	0.3659 (8)	0.2942 (7)	0.1541 (5)
C(48)	0.3088 (8)	0.4471 (7)	0.1095 (5)
C(22)	0.1770 (6)	0.1076 (5)	0.1019 (4)
C(23)	0.2563 (7)	0.0775 (7)	0.1458 (5)
C(24)	0.2531 (8)	0.0751 (7)	0.2160 (6)
C(25)	0.1722 (8)	0.1048 (7)	0.2466 (5)
C(26)	0.0962 (8)	0.1358 (6)	0.2081 (5)
C(27)	0.0932 (7)	0.1386 (5)	0.1313 (4)
C(28)	0.1856 (6)	0.1026 (5)	0.0276 (4)
C(32)	−0.1880 (8)	0.2069 (7)	−0.0990 (6)
C(33)	−0.2658 (8)	0.2091 (8)	−0.1489 (6)
C(34)	−0.3482 (9)	0.1697 (9)	−0.1341 (7)
C(35)	−0.3587 (7)	0.1233 (7)	−0.0726 (6)
C(36)	−0.2832 (6)	0.1175 (6)	−0.0233 (5)
C(37)	−0.1986 (6)	0.1569 (6)	−0.0362 (5)
C(38)	−0.1081 (7)	0.2572 (7)	−0.1141 (5)
C(51)	0.1462 (6)	0.1059 (7)	−0.0950 (4)
C(52)	0.1758 (8)	0.1992 (8)	−0.1271 (6)
C(53)	0.1016 (8)	0.2701 (7)	−0.1559 (5)
C(54)	0.0465 (8)	0.3234 (7)	−0.1053 (5)
C(55)	0.2322 (7)	0.0384 (8)	−0.0985 (6)
C(56)	0.0593 (7)	0.0619 (6)	−0.1320 (5)
C(57)	0.1073 (7)	0.3572 (7)	−0.0395 (5)
C(58)	0.0027 (9)	0.4099 (8)	−0.1403 (7)

[a] The estimated error in the last digit is given in parentheses. This form is used throughout. [b] The numbering scheme is shown in Figure 1. [c] The equivalent positions for the space group Cc are the following: $x, y, z; x, \bar{y}, {}^1/_2 + z$ (0, 0, 0 and $^1/_2$, $^1/_2$, 0).

$C2/c$ or Cc for the monoclinic cell. The approximate cell constants were a = 14.40 (4) Å, b = 14.41 (9) Å, c = 19.37 (3) Å, and β = 94.1 (2)°. A second, smaller crystal in the form of a rectangular parallelepiped with mean dimensions of 0.23 × 0.14 × 0.38 mm was mounted on a glass fiber with the long dimension parallel to the fiber axis. This crystal was placed on a Syntex $P\bar{1}$ diffractometer and optically centered. Precise cell constants were determined by least-squares refinement using the 2θ values of 15 pairs of reflections measured at $+2\theta$ and -2θ values in the range 4–12°. They are a = 14.374 (7) Å, b = 14.508 (3) Å, c = 19.370 (3) Å, and β = 94.33 (8)°. Partial oscillation photographs (±14°) were taken about each of the crystal axes to check crystal quality and the correctness of indexing. With the assumption of eight formula units per unit cell, the calculated density is 1.37 g cm^{-3} and the measured density 1.33 (3) g cm^{-3} (neutral buoyancy in CCl_4/heptane). All measurements were made at room temperature.

Table II. Root-Mean-Square Displacements (Å)

atom	min	mean	max	atom	min	mean	max
Cu(1)	0.185	0.213	0.228	Cu(2)	0.193	0.211	0.224
O(1)	0.199	0.253	0.274	O(21)	0.189	0.210	0.250
O(11)	0.213	0.244	0.270	O(31)	0.196	0.238	0.313
N(9)	0.186	0.207	0.244	N(29)	0.183	0.199	0.226
N(19)	0.187	0.209	0.219	N(39)	0.195	0.209	0.251
C(2)	0.184	0.238	0.306	C(22)	0.155	0.208	0.227
C(3)	0.225	0.289	0.336	C(23)	0.220	0.229	0.258
C(4)	0.218	0.310	0.353	C(24)	0.236	0.258	0.278
C(5)	0.216	0.267	0.378	C(25)	0.218	0.244	0.287
C(6)	0.186	0.248	0.333	C(26)	0.203	0.252	0.262
C(7)	0.177	0.241	0.304	C(27)	0.164	0.207	0.235
C(8)	0.212	0.225	0.247	C(28)	0.181	0.225	0.232
C(12)	0.175	0.209	0.248	C(32)	0.217	0.240	0.269
C(13)	0.218	0.240	0.283	C(33)	0.206	0.286	0.324
C(14)	0.203	0.267	0.334	C(34)	0.237	0.303	0.325
C(15)	0.212	0.222	0.335	C(35)	0.215	0.221	0.283
C(16)	0.187	0.218	0.320	C(36)	0.168	0.207	0.276
C(17)	0.183	0.221	0.239	C(37)	0.194	0.209	0.238
C(18)	0.185	0.192	0.235	C(38)	0.199	0.220	0.266
C(41)	0.175	0.203	0.253	C(51)	0.186	0.200	0.264
C(42)	0.196	0.247	0.254	C(52)	0.217	0.245	0.292
C(43)	0.185	0.210	0.257	C(53)	0.210	0.245	0.294
C(44)	0.191	0.211	0.251	C(54)	0.188	0.242	0.259
C(45)	0.210	0.282	0.317	C(55)	0.196	0.246	0.286
C(46)	0.206	0.246	0.267	C(56)	0.203	0.229	0.278
C(47)	0.213	0.249	0.265	C(57)	0.214	0.240	0.292
C(48)	0.231	0.253	0.277	C(58)	0.219	0.308	0.336

Intensity measurements were made as previously described[13] for the 2768 reflections with $2\theta \leq 45°$ in the forms hkl and $hk\bar{l}$.

From these data 2645 unique reflections were obtained. The θ–2θ scan for these measurements, using Mo Kα radiation (λ 0.71069 Å) and a graphite monochromator, was from 0.7° below to 0.7° above the reflection in 2θ. Scan rates varied from 1.0 to 4.0°/min depending on the intensity of the reflection. Four standard reflections were used to check stability and to account for long-term drift. The drift correction varied from 1.057 to 0.999. Since μ, the linear absorption coefficient, was 11.20 cm^{-1}, absorption corrections were applied. The transmission coefficients ranged from 0.953 to 0.810. The correctness[14] of the calculations of transmission coefficients was checked by a series of ψ scans of the standard reflections. Of the set of 2645 unique normalized structure factors, 2424 had $F_o^2 \geq 2\sigma(F_o^2)$, where a value of 0.04 was used for p, the ignorance factor[13] in calculating $\sigma(F_o^2)$.

Both the statistical distribution[15] of E values and piezoelectric tests[16] strongly suggested that the acentric space group Cc was the correct choice. A sharpened origin-removed Patterson map indicated positions for the copper atoms compatible with the acentric space group. An electron density synthesis based on phases derived from the copper positions revealed the positions of the remaining nonhydrogen atoms. On convergence of refinement with isotropic thermal parameters, the proper choice of enantiomers was tested by changing all y coordinates to their negatives and refining the mirrored model to convergence. The original model had converged[17] to R_1 = 0.071, whereas the alternative model converged to R_1 = 0.074. Refinement of the original model was continued with anisotropic thermal parameters and converged to R_1 = 0.049 and R_2 = 0.055. In the final cycle of refinement, the average shift per error was 0.033.

A total of 2424 reflections was used to refine 485 variables. A final difference map was essentially featureless with the highest peak less than 0.6 e Å^{-3}. Examination of groups of reflections ordered on $(\sin\theta)/\lambda$ or on $|F_o|$ revealed no significant trends in disagreement with the model. Zerovalent scattering curves from Cromer[18] were used for Cu, O, N, and C. Those for hydrogen were taken from Stewart.[19] Corrections for anomalous dispersion[20] were made using $\Delta f'$ = 0.263 and $\Delta f''$ = 1.266 for Cu. The values of $|F_o|$ and F_c are listed in Table A.[21]

Results and Discussion

Fractional atomic positional parameters of the nonhydrogen atoms from the last cycle of refinement are presented in Table I. Anisotropic thermal parameters are listed in Table B. The derived root-mean-square displacements are given in Table II and the associated thermal ellipsoids (50% probability) are illustrated in Figure 1. Bond distances and angles have been

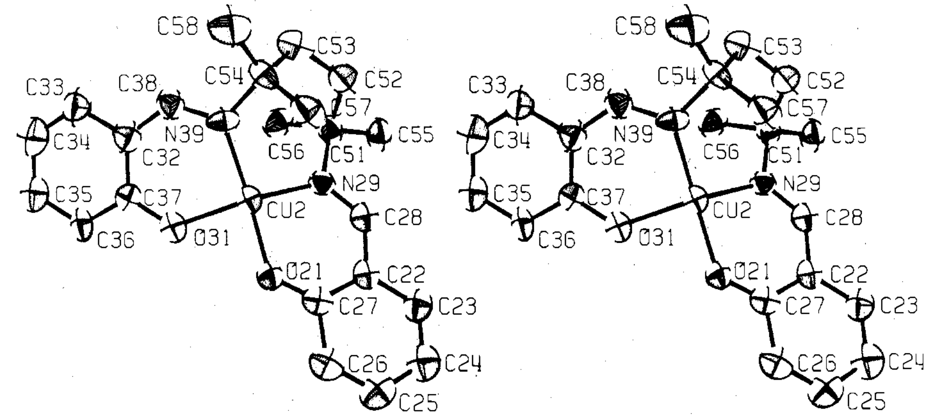

Figure 1. A stereoview of one of the two Cu(sal$_2$tmput) molecules.

Table III. Bond Lengths (Å)

Cu(1)–O(1)	1.893 (6)	C(2)–C(3)	1.41 (3)
Cu(1)–O(11)	1.90 (4)	C(3)–C(4)	1.43 (2)
Cu(1)–N(9)	1.98 (9)	C(4)–C(5)	1.38 (6)
Cu(1)–N(19)	1.98 (1)	C(6)–C(7)	1.44 (1)
Cu(2)–O(21)	1.88 (3)	C(7)–C(2)	1.48 (6)
Cu(2)–O(31)	1.91 (2)	C(12)–C(13)	1.44 (3)
Cu(2)–N(29)	1.97 (3)	C(13)–C(14)	1.38 (2)
Cu(2)–N(39)	1.98 (3)	C(14)–C(15)	1.40 (2)
O(1)–C(7)	1.29 (3)	C(15)–C(16)	1.39 (3)
O(11)–C(17)	1.33 (2)	C(16)–C(17)	1.40 (2)
O(21)–C(27)	1.25 (5)	C(17)–C(12)	1.42 (2)
O(31)–C(37)	1.30 (6)	C(22)–C(23)	1.44 (6)
N(9)–C(8)	1.29 (2)	C(23)–C(24)	1.36 (2)
N(9)–C(41)	1.51 (2)	C(24)–C(25)	1.41 (4)
N(19)–C(18)	1.30 (3)	C(25)–C(26)	1.35 (5)
N(19)–C(44)	1.54 (1)	C(26)–C(27)	1.48 (1)
N(29)–C(28)	1.30 (6)	C(27)–C(22)	1.44 (4)
N(29)–C(51)	1.53 (3)	C(32)–C(33)	1.42 (7)
N(39)–C(38)	1.30 (5)	C(33)–C(34)	1.36 (3)
N(39)–C(54)	1.51 (3)	C(34)–C(35)	1.39 (2)
C(2)–C(8)	1.45 (1)	C(35)–C(36)	1.39 (6)
C(12)–C(18)	1.43 (1)	C(36)–C(37)	1.38 (2)
C(22)–C(28)	1.45 (2)	C(37)–C(32)	1.44 (2)
C(32)–C(38)	1.41 (2)	C(41)–C(42)	1.55 (4)
C(41)–C(45)	1.58 (5)	C(42)–C(43)	1.53 (4)
C(44)–C(47)	1.53 (2)	C(43)–C(44)	1.52 (4)
C(51)–C(55)	1.58 (2)	C(51)–C(52)	1.56 (2)
C(54)–C(57)	1.57 (6)	C(52)–C(53)	1.56 (4)
C(41)–C(46)	1.55 (2)	C(53)–C(54)	1.52 (5)
C(44)–C(48)	1.54 (1)		
C(51)–C(56)	1.53 (5)		
C(54)–C(58)	1.54 (3)		

Table IV. Bond Angles (deg)

C(2)–C(3)–C(4)	118 (1)	C(12)–C(13)–C(14)	119 (1)
C(3)–C(4)–C(5)	123 (1)	C(13)–C(14)–C(15)	120 (1)
C(4)–C(5)–C(6)	120 (1)	C(14)–C(15)–C(16)	121 (1)
C(5)–C(6)–C(7)	120 (1)	C(15)–C(16)–C(17)	119 (1)
C(6)–C(7)–C(2)	118.6 (9)	C(16)–C(17)–C(12)	120 (1)
C(7)–C(2)–C(3)	119.5 (9)	C(17)–C(12)–C(13)	119.0 (9)
C(22)–C(23)–C(24)	120.8 (9)	C(32)–C(33)–C(34)	120 (1)
C(23)–C(24)–C(25)	120 (1)	C(33)–C(34)–C(35)	122 (1)
C(24)–C(25)–C(26)	122 (1)	C(34)–C(35)–C(36)	119 (1)
C(25)–C(26)–C(27)	121 (1)	C(35)–C(36)–C(37)	120.1 (9)
C(26)–C(27)–C(22)	115.2 (8)	C(36)–C(37)–C(32)	120.9 (9)
C(27)–C(22)–C(23)	120.6 (8)	C(37)–C(32)–C(33)	117 (1)
O(1)–C(7)–C(6)	118.7 (9)	C(8)–C(2)–C(3)	116 (1)
O(11)–C(17)–C(16)	118 (1)	C(18)–C(12)–C(13)	114.8 (9)
O(21)–C(27)–C(26)	120.2 (9)	C(28)–C(22)–C(23)	116.6 (8)
O(31)–C(37)–C(36)	119.2 (8)	C(38)–C(32)–C(33)	117 (1)
O(1)–C(7)–C(2)	122.8 (8)	C(8)–C(2)–C(7)	124.2 (9)
O(11)–C(17)–C(12)	121.9 (9)	C(18)–C(12)–C(17)	126.1 (9)
O(21)–C(27)–C(22)	124.5 (8)	C(28)–C(22)–C(27)	120.6 (8)
O(31)–C(37)–C(32)	119.9 (9)	C(38)–C(32)–C(37)	125.3 (9)
C(2)–C(8)–N(9)	125.4 (9)	C(8)–N(9)–C(41)	117.2 (8)
C(12)–C(18)–N(19)	126.6 (8)	C(18)–N(19)–C(44)	118.0 (7)
C(22)–C(28)–N(29)	126.2 (8)	C(28)–N(29)–C(51)	115.7 (7)
C(32)–C(38)–N(39)	128.5 (9)	C(38)–N(39)–C(54)	117.9 (8)
N(9)–C(41)–C(42)	108.2 (8)	N(19)–C(44)–C(43)	108.2 (8)
N(9)–C(41)–C(45)	110.9 (8)	N(19)–C(44)–C(47)	106.6 (7)
N(9)–C(41)–C(46)	107.3 (7)	N(19)–C(44)–C(48)	109.4 (7)
C(42)–C(41)–C(45)	108.9 (8)	C(43)–C(44)–C(47)	114.4 (8)
C(42)–C(41)–C(46)	115.1 (8)	C(43)–C(44)–C(48)	109.3 (7)
C(45)–C(41)–C(46)	106.4 (9)	C(47)–C(44)–C(48)	108.8 (8)
N(29)–C(51)–C(52)	108.5 (8)	N(39)–C(54)–C(53)	108.3 (8)
N(29)–C(51)–C(55)	112.4 (7)	N(39)–C(54)–C(57)	106.3 (8)
N(29)–C(51)–C(56)	105.7 (9)	N(39)–C(54)–C(58)	111.7 (9)
C(52)–C(51)–C(55)	106.4 (8)	C(53)–C(54)–C(57)	113.5 (9)
C(52)–C(51)–C(56)	114.4 (8)	C(53)–C(54)–C(58)	110.4 (9)
C(55)–C(51)–C(56)	109.6 (8)	C(57)–C(54)–C(58)	106.7 (8)
C(41)–C(42)–C(43)	120.6 (8)		
C(42)–C(43)–C(44)	120.1 (8)		
C(51)–C(52)–C(53)	121.0 (9)		
C(52)–C(53)–C(54)	118.9 (8)		
N(9)–Cu(1)–O(1)	95.6 (3)	N(29)–Cu(2)–O(21)	95.3 (3)
N(19)–Cu(1)–O(11)	95.5 (3)	N(39)–Cu(2)–O(31)	93.9 (3)
N(9)–Cu(1)–O(11)	143.4 (4)	N(29)–Cu(2)–O(31)	145.4 (3)
N(19)–Cu(1)–O(1)	143.0 (3)	N(39)–Cu(2)–O(21)	146.5 (3)
N(19)–Cu(1)–N(9)	101.9 (3)	N(39)–Cu(2)–N(29)	101.8 (3)
O(11)–Cu(1)–O(1)	89.2 (3)	O(31)–Cu(2)–O(21)	87.8 (3)

gathered in Tables III and IV.

Crystal Structure of Cu(sal$_2$tmput). The crystal consists of asymmetric pairs of Cu(sal$_2$tmput) molecules, four pairs to the unit cell. The Cu(sal$_2$tmput) molecules have D_{2d}-distorted tetrahedral geometry, the coordination sphere being comprised of two imine nitrogen atoms and two phenolic oxygen atoms from the sal$_2$tmput ligand.

The two independent Cu(sal$_2$tmput) molecules have essentially identical structures, including the chirality of wrapping the tetradentate ligand about the copper atom. Each copper atom is strictly four-coordinate. There are no other Cu–O or Cu–N approaches of less than 4.0 Å. The neutral molecules pack together with normal van der Waals contacts. The similarity of the two independent molecular structures indicates that the distorted tetrahedral geometry is likely to persist in solution and is not merely an artifact of crystal packing.

It may be seen from Tables III and IV that no unusual bond lengths or angles were found in the sal$_2$tmput ligand. The introduction of methyl substituents on the butylenediimine backbone disrupts the planar configuration otherwise expected about the copper center. The distortion involves the twisting of the ligand planes in opposite directions resulting in a D_{2d}-distorted tetrahedral geometry about the copper atom. The equations of the least-squares planes through the phenyl rings and the atom deviations are given in Table V. The dihedrals defined by the phenyl moieties bound to Cu(1) and Cu(2) are 52.4 and 45.6°, respectively, whereas they would be 90° for tetrahedral coordination and 0° for square planar.

Structural comparisons of Cu(sal$_2$tmput) with Cu(sal$_2$en) and Cu(t-Bu-sal)$_2$ show expected similarities. Copper–nitrogen and copper–oxygen bond lengths are quite similar as are the

Table V. Least-Squares Planes

atom	dev[a]	atom	dev	atom	dev
Ring 1					
C(2)	0.003	C(3)	−0.004	C(4)	0.001
C(5)	0.004	C(6)	−0.005	C(7)	0.001
Ring 2					
C(12)	0.012	C(13)	−0.000	C(14)	−0.008
C(15)	0.005	C(16)	0.008	C(17)	−0.016
Ring 3					
C(22)	−0.007	C(23)	0.012	C(24)	−0.006
C(25)	−0.005	C(26)	0.08	C(27)	−0.007
Ring 4					
C(32)	0.020	C(33)	−0.016	C(34)	0.004
C(35)	0.004	C(36)	0.002	C(37)	−0.014

Equations of Planes

ring 1: $-10.635x + 4.285y + 12.758z = -3.927$
ring 2: $13.509x + 4.942y - 1.864z = 7.007$
ring 3: $5.118x + 13.538y + 0.446z = 2.414$
ring 4: $-4.631x + 12.340y + 8.499z = 2.562$

[a] These are the deviations of the atoms in angstroms from the calculated plane.

bond lengths and angles of the salicylaldiminato residues.[8-10]

The most apparent structural differences are found in the copper–ligand bond angles and the dihedral angles defined by the phenyl rings in the respective compounds. In the case of Cu(sal$_2$en), the ethylene bridge allows essentially planar coordination about the copper center, resulting[10] in a dihedral of approximately 0°. However, the presence of methyl substituents prevents the putrescine backbone from attaining a similar conformation resulting in a dihedral averaging 49° for Cu(sal$_2$tmput). The structure of Cu(*t*-Bu-sal)$_2$, which differs from the Cu(sal$_2$tmput) species only in lacking a bond between two methyl carbons of the *tert*-butyl substituents, exhibits[8] a dihedral of 61.9. However, the N–Cu–N and O–Cu–O bond angles are 139.7 (2) and 131.1 (2)°, respectively, for Cu(*t*-Bu-sal)$_2$ compared to 101.8 (3) and 88.5 (3)° for Cu(sal$_2$tmput). Thus the putrescine bridge not only forces a distorted tetrahedral environment but also encapsulates the metal ion.

The tetrahedral structure of the complex enhances the ease of reduction of Cu(II) to Cu(I). The $E^{\circ\prime}$ value of −0.722 V determined for this complex is significantly less negative than the value of −1.081 V found[7] for Cu(sal$_2$en) which has planar coordination about the copper atom. Cu(sal$_2$tmput) has the distorted type of tetrahedral structure which has been recently discovered[22] for plastocyanin, although it contains two phenolate oxygen atoms in place of the cysteine and methionine sulfur atoms of that protein. It has the advantage of the additional stability associated with a single tetradentate ligand compared to two bidentate ligands in Cu(*t*-Bu-sal)$_2$.

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Registry No. Cu(sal$_2$tmput), 68975-43-9; sal$_2$tmputH$_2$, 67360-22-9; salicylaldehyde, 90-02-8; 2,5-dimethylhexane-2,5-diamine, 23578-35-0.

Supplementary Material Available: Tables A and B giving $|F_o|$ and F_c and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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