knowledged. The collaboration between The Ohio State University and the University of Warwick has been supported by a NATO travel grant.

Supplementary Material Available: Tables S1-S8, listing selected infrared bands, NMR chemical shift values, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and temperature factors (9 pages); Table S9, listing structure factors (8 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department,
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Synthesis, Electron Spin Resonance Spectroscopy, and Shape-Determining Angle Analysis of Superstructured Copper(II) Schiff Base Complexes Containing Persistent Voids

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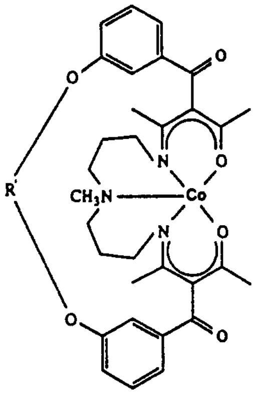
Syntheses, electron spin resonance spectroscopy, X-ray structural determinations, and shape-determining angle analyses for the five-coordinate Schiff base complexes [Cu(Me$_2$H$_2$Me$_2$malMeDPT)], [Cu{Me$_2$(C3)Me$_2$malMeDPT}], and [Cu{Me$_2$(C6)-Me$_2$malMeDPT}] are reported. Syntheses of the superstructured complexes are accomplished by utilizing high-dilution techniques. Interpretation of the ESR spectra suggests that the complexes are five-coordinate with geometries intermediate between TBP and SP. This interpretation is supported by the X-ray structure of each complex. [Cu(Me$_2$H$_2$Me$_2$malMeDPT)] crystallizes in the monoclinic system ($C2/c$) with unit cell dimensions a = 17.746 (3) Å, b = 7.108 (1) Å, c = 17.278 (2) Å, β = 121.68 (1)°, and Z = 4. A total of 2046 reflections were collected, 1662 with $I > 3\sigma(I)$. The structure was refined to weighted and unweighted R factors of 4.2 and 4.0%, respectively. [Cu{Me$_2$(C3)Me$_2$malMeDPT}] crystallizes in the orthorhombic system ($Pbca$) with unit cell dimensions a = 9.758 (1) Å, b = 35.922 (2) Å, and c = 17.899 (2) Å. With 2960 reflections having intensities greater than $3\sigma(I)$, the structure was refined to weighted and unweighted R factors of 6.0 and 5.2%, respectively. [Cu{Me$_2$(C6)Me$_2$malMeDPT}] crystallizes in the triclinic system ($P\bar{1}$) with unit cell dimensions a = 11.437 (1) Å, b = 13.374 (1) Å, c = 13.611 Å, α = 101.02 (1)°, β = 116.73 (1)°, and γ = 101.14 (1)°. Weighted and unweighted R factors are 4.1 and 4.3%, respectively, for 3991 reflections with $I > 3\sigma(I)$.

Introduction

In a preliminary communication[1] we reported the successful design and synthesis of cobalt(II) dioxygen carriers of the structure I. Central to this work on dioxygen carriers is the principle of inclusion chemistry and the fundamental guest-host interaction of the O$_2$ molecule with the lacunar carrier complex.[2] The copper complexes that we report here serve as the direct precursors to the host cobalt complexes. Their structural analyses are important, not only in the designing ideal host molecules for dioxygen but also for demonstrating the ability to create structures with variable persistent voids.[3]



I

The complex [Cu(Me$_2$H$_2$Me$_2$malMeDPT)][4] was first prepared by Cummings et al.[5] and was thoroughly characterized with the exception of an X-ray structural determination. The structure of this related unbridged complex (II in Scheme I) is reported herein for comparison to the superstructured copper complexes (III in Scheme I). All three structures display coordination geometries about copper that are intermediate between trigonal bipyramidal (TBP) and square pyramidal (SP). Muetterties[6] has refined a method for more precisely describing these intermediate geometries via reference to idealized polyhedra. These *shape-determining angles* about a coordination sphere define the mo-

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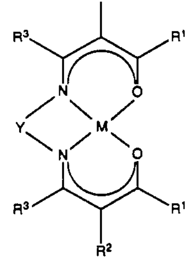
[1] Delgado, R.; Glogowski, M. W.; Busch, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 6855.

[2] (a) Busch, D. H.; Stephenson, N. A. *J. Inclusion. Phenom. Recognit. Chem.* **1989**, *7*, 137. (b) Busch, D. H. Synthetic Dioxygen Carriers for Dioxygen Transport. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum Publishing Corp.: New York, 1988.

[3] (a) Atwood, J. L.; Davies, J. E. D., Eds. *Inclusion Phenomena in Inorganic, Organic and Organometallic Hosts*; D. Reidel Publishing Co.: Boston, MA, 1987. (b) Meade, T. J.; Busch, D. H. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1985; Vol. 33, p 59. (c) Alcock, N. W.; Lin, W.-K.; Cairns, C.; Pike, G. A.; Busch, D. H. *J. Am. Chem. Soc.* **1989**, *111*, 6630.

[4] We have chosen to name complexes of this type in a consistent manner (Goldsby, K. A.; Jircitano, A. J.; Minahan, D. M.; Ramprasad, D.; Busch, D. H. *Inorg. Chem.* **1987**, *26*, 2651) based on the structure



[M(R$^1_2$R$^2_2$R$^3_2$malY)]

[5] Chen, Y.; Chu, D. E.; McKinney, B. D.; Willis, L. J.; Cummings, S. C. *Inorg. Chem.* **1981**, *20*, 1885, 3582.

[6] Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

* To whom correspondence should be addressed at the Chemistry Department, The University of Kansas, Lawrence, KS 66045.

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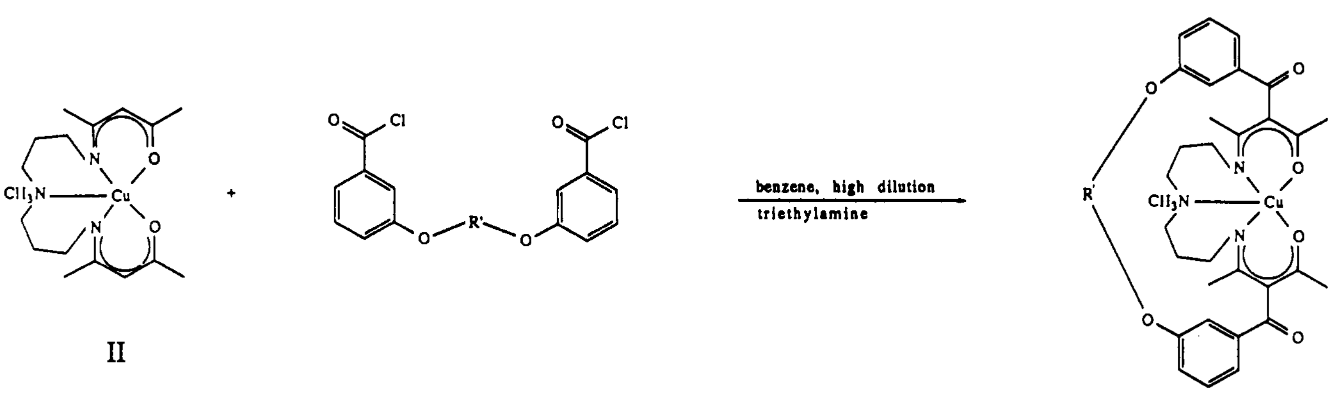
Scheme I



II

III

lecular shape and obviate ambiguous language regarding geometry.

Experimental Section

Materials. All metal salts, organic reagents, and solvents were reagent grade. Solvents were dried by following recommended procedures.[7] A general preparation for the synthesis of the bridging reagent has been described previously.[8]

Physical Measurements. ^{13}C NMR spectra were obtained by using a Bruker AM-250 Fourier transform spectrometer operating at 62.896 MHz. Infrared spectra were obtained with a Perkin-Elmer Model 283B recording spectrophotometer operating in the range 4000–200 cm^{-1}. Mass spectra were obtained on a Kratos MS-30 mass spectrometer utilizing fast atom bombardment techniques and a matrix composed of a 3:1 mixture of dithiothreitol and dithioerythritol (denoted FAB-MB).

Electron spin resonance spectra were recorded with a Varian E-line Century Series spectrometer equipped with a liquid-nitrogen-insert dewar. Magnetic flux density corrections for samples were made with strong pitch (0.1%) as an external standard (g = 2.0028). Solution samples were run as frozen glasses of 1:1 benzene/toluene by volume at −196 °C in quartz tubes.

Pentadentate Schiff Base Complexes. (4,4'-Methyl-4-aza-1,7-heptanediyldinitrilo-κ^3N)bis(2-pentanonato-κ^2O))nickel(II), [Cu(Me$_2$H$_2$Me$_2$malMeDPT)]. This complex was prepared by the known literature method[5] and was recrystallized from hexane.

(7,19-Diacetyl-6,20-Dioxo-8,13,18-trimethyl-26,33-dioxa-9,13,17-triazatricyclo[23.8.1^{1,5}.1^{21,25}]pentatriaconta-1,3,5(34),7,18,21,23,25(35)-octaenato-κ^3N,κ^2O)copper(II), [Cu{Me$_2$(C6)Me$_2$malMeDPT}]. Dry benzene (1.5 L) was distilled into a two-liter three-necked flask, and 1.0 mL of triethylamine was added. A solution of 1.051 g (2.833 mmol) of the corresponding unbridged copper complex, [Cu(Me$_2$H$_2$Me$_2$malMeDPT)], and a solution of 1.121 g (2.836 mmole) of the C6 acid chloride,[8] each in dry benzene (100 mL), were prepared. The two solutions were added simultaneously via a syringe pump to the 1.5-L reservoir of benzene at room temperature. Addition was adjusted to a rate of 2 mL/h or approximately over a period of 2 days. The mixture was stirred for a period of 5 days and then filtered to remove the white precipitate of triethylamine hydrochloride. The filtrate was concentrated on a rotary evaporator to a volume of 50 mL, and then 20 mL of cyclohexane was added. An unidentified precipitate was removed by filtration and discarded. The resulting filtrate was concentrated, and an emerald green precipitate began to form. The solids were collected after 1 night in the refrigerator. Yield: 53%. Infrared spectrum (KBr pellet, cm^{-1}): ν(CO) 1650, 1640 (s); ν(CN,CC) 1580 (s, br).

(7,19-Diacetyl-6,20-dioxo-8,13,17-trimethyl-26,30-dioxa-9,13,17-triazatricyclo[23.5.1^{1,5}.1^{21,25}]dotriaconta-1,3,5(31),7,18,21,23,25(32)-octaenato-κ^3N,κ^2O)copper(II), [Cu{Me$_2$(C3)Me$_2$malMeDPT}]. This complex was prepared in a manner analogous to that for the C6-bridged compound with one exception: The initial reaction filtrate was concentrated to 40 mL, and 30 mL of cyclohexane was added. Yield: 54%. Infrared spectrum (KBr pellet, cm^{-1}): ν(CO) 1640 (s); ν(CN,CC) 1580 (s, br).

Growth and Selection of X-ray-Quality Crystals. [Cu(Me$_2$H$_2$Me$_2$malMeDPT)]. Crystals suitable for X-ray studies were obtained by slow cooling of a hexane solution. A bright green parallelepipedon of dimensions 0.24 × 0.16 × 0.55 mm^3 was mounted with epoxy resin on a glass fiber in a random orientation for data collection.

[Cu{Me$_2$(C6)Me$_2$malMeDPT}], (C6). A chloroform solution of the (C6) complex was layered with acetonitrile. After several weeks, bright green hexagonal-shaped crystals were isolated. A crystal 0.12 × 0.23 × 0.50 mm^3 was selected for data collection and mounted on a glass fiber with epoxy resin in a random orientation.

[Cu{Me$_2$(C3)Me$_2$malMeDPT}], (C3). Suitable crystals of the (C3) complex were obtained by slow diffusion of diethyl ether into a concentrated chloroform solution of the compound. A green platelike crystal was cut to dimensions of 0.12 × 0.46 × 0.46 mm^3 and mounted in a random orientation for data collection.

Collection and Reduction of the Diffraction Data. For both the unbridged and the (C6) complexes, preliminary examination and diffraction data collection were performed with Mo Kα radiation (λ = 0.71069 Å) on a Syntex (Nicolet) P$\bar{1}$ diffractometer equipped with a graphite-crystal incident-beam monochromater. Cell constants and an orientation matrix for data collection were obtained at ambient temperature from the least-squares refinement of the setting angles of 25 reflections in the range 20° < 2θ < 30°.

The unbridged complex crystallizes in the monoclinic crystal system, and Z = 4. From an inspection of the systematic absences, hkl, $h + k = 2n$, $h0l$, $l = 2n$, the space group was determined to be either $C2/c$ or Cc. On the basis of the successful solution of the structure in space group $C2/c$ and the unsuccessful elimination of the disorder (vide infra) in Cc, the former was chosen. Data were collected in the $+h,+k,\pm l$ quadrant in the range 4° < 2θ < 50° by using the θ–2θ-scan technique and a variable scan rate. The data were corrected for Lorentz and polarization effects.

The (C6) complex is triclinic, space group $P\bar{1}$, and data were collected by using the θ–2θ scan technique between the limits 4° < 2θ < 50.1° in the $+h,\pm k,\pm l$ hemisphere at a variable scan rate and were corrected for Lorentz and polarization effects.

The crystal data for the (C3) complex were collected by using Mo Kα radiation on a Rigaku AFC5S diffractometer equipped with a graphite-crystal incident-beam monochromator. Cell constants and an orientation matrix were obtained from the least-squares refinement of 25 reflections between the range 20° < 2θ < 30°. The (C3) complex crystallizes in the orthorhombic crystal system; the space group is uniquely determined from the systematic absences, $0kl$, $k = 2n$, $h0l$, $l = 2n$, $hk0$, $h = 2n$, to be $Pbca$. Data were collected at ambient temperature in the $+h,+k,+l$ octant by using the ω-scan technique at a scan speed of 6°/min in ω with a maximum of six scans per reflection. The data were corrected for absorption, by using the PSI scan technique, as well as for Lorentz and polarization effects.

For all three structures, the intensities of six standard reflections were measured every 100 reflections as a check on crystal quality. No decomposition over the time period of data collection was observed. Table I summarizes the details of data collection for all three structures.

Solution and Refinement of the Structures. The structure of the unbridged complex was solved by using the Patterson heavy-atom method, which revealed the location of the copper atom. The coordinates for the remaining non-hydrogen atoms were located by successive least-squares and difference Fourier techniques, using SHELX-76.[9]

The copper atoms in both the (C6) and (C3) complexes were located by using the Patterson function. DIRDIF, a modified direct methods procedure, then utilized the copper coordinates to phase the structure so that the remaining non-hydrogen atoms were located. The structures

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[7] Perrins, D. D.; Armarego, W. L. F.; Perrins, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, England, 1980.

[8] Ramprasad, D.; Lin, W.-K.; Goldsby, K. A.; Busch, D. H. *J. Am. Chem. Soc.* **1988**, *110*, 1480.

[9] Sheldrick, G. M. SHELX-76, 1983.

Table I. Data Collection and Refinement Details

	unbridged	(C_6)	(C_3)
empirical formula	$CuO_2N_3C_{17}H_{29}'$	$CuO_6N_3C_{37}H_{47}$	$CuO_6N_3C_{34}H_{41}$
fw	379.98	693.34	651.26
cryst system	monoclinic	triclinic	orthorhombic
space group	*C*2/*c*	$P\bar{1}$	*Pbca*
a, Å	17.746 (1)	11.437 (1)	9.758 (1)
b, Å	7.108 (1)	13.374 (1)	35.922 (2)
c, Å	17.278 (1)	13.611 (1)	17.899 (2)
α, deg	90.0	101.02 (1)	90.0
β, deg	121.68 (1)	116.73 (1)	90.0
γ, deg	90.0	101.14 (1)	90.0
V, Å^3	1854.7 (x)	1730.1 (8)	6274 (2)
Z	4	2	8
density(calcd), g/cm^3	1.36	1.31	1.38
μ(Mo Kα), cm^{-1}	11.34	7.08	7.77
diffractometer	Syntex P1	Syntex P1	Rigaku AFC5S
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp, °C	19	19	23
2θ(max), deg	50	50.1	55.1
no. of observns ($I > 3.0\sigma(I)$)	1662	3991	2960
no. of variables	119	451	442
residuals: R; R_w	0.040; 0.042	0.043; 0.041	0.052; 0.060
largest resid electron dens peak, e/Å^3	0.64	0.46	0.41

Table II. Positional Parameters for [Cu($Me_2H_2Me_2$malMeDPT)]

atom	*x*	*y*	*z*
Cu	0.00000 (0)	−0.13988 (6)	0.25000 (0)
O1	0.09730 (14)	−0.22009 (32)	0.23476 (15)
N1	−0.08219 (15)	−0.12059 (32)	0.11808 (15)
N2	0.00000 (0)	0.19621 (42)	0.25000 (0)
C1	−0.16057 (19)	−0.00794 (50)	0.09449 (20)
C2	−0.14255 (22)	0.20208 (54)	0.09788 (25)
C3A	−0.04224 (39)	0.26725 (91)	0.15457 (41)
C3B	−0.09115 (39)	0.26627 (96)	0.20192 (43)
C4	0.04962 (46)	0.26496 (98)	0.20810 (50)
C11	−0.13613 (28)	−0.15102 (56)	−0.04554 (22)
C12	−0.06755 (23)	−0.17884 (40)	0.05494 (20)
C13	0.01328 (24)	−0.26535 (43)	0.07639 (23)
C14	0.08816 (24)	−0.27536 (40)	0.15954 (25)
C15	0.17301 (29)	−0.35483 (50)	0.17070 (32)
H71B	0.3292	0.2319	0.0818

were subsequently refined by using the TEXSAN system of computer programs.[10]

For all three structures, refinement was accomplished by full-matrix least-squares techniques where the function minimized was $\sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. In the final refinement cycles, anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atom positions were calculated by assuming idealized geometries and standard C–H bond distances of 0.95 Å. The hydrogen atom positions were included in structure factor calculations, but their parameters were not refined. Final difference Fourier maps were essentially featureless with the residual electron density located in the vicinity of the disordered dipropylmethylamine bridges (vide infra). The final agreement factors and largest residual peak heights for all three structures are also presented in Table I. The positional parameters for all non-hydrogen atoms are presented in Tables II–IV for the unbridged, (C6), and (C3) structures, respectively.

Results and Discussion

Synthesis and Characterization of [Cu{Me_2(C6)Me_2malMeDPT}] and [Cu{Me_2(C3)Me_2malMeDPT}]. The superstructured copper complexes were prepared in essentially the same manner (Scheme I) by reacting the parent copper complex with the appropriate acid chloride under conditions of high dilution. Triethylamine serves as a catalyst for the acylation and as a base to neutralize the HCl produced during reaction. Dry solvent is used for reaction and workup because of the sensitivity of these complexes to moisture. The infrared spectrum of the green product displays a carbonyl stretch at 1650 cm^{-1} in each case, differentiating them from the starting acid chlorides, which show carbonyl stretches at 1760 cm^{-1}.

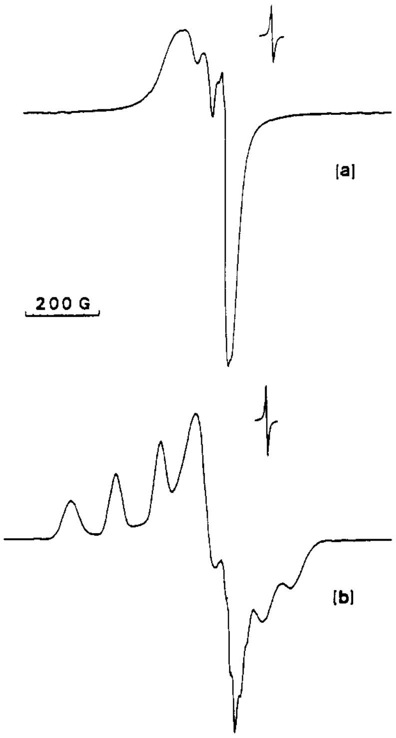

Figure 1. Isotropic (a) and anisotropic (b) ESR spectra in 1:1 benzene/toluene for [Cu($Me_2H_2Me_2$malMeDPT)].

ESR Spectroscopy. The solution and frozen glass ESR spectral data for the three complexes are reported in Table V. The isotropic and anisotropic ESR spectra for [Cu($Me_2H_2Me_2$malMeDPT)] are shown in Figure 1, and the corresponding spectra for [Cu{Me_2(C3)Me_2malMeDPT}] are shown in Figure 2. Spectra for [Cu{Me_2(C6)Me_2malMeDPT}] are very similar to the C3-bridged complex and are not reproduced here. The bridged complexes display nearly axial spectra at 77 K with g_1 and g_2 not clearly resolved and A_3 = 141 G. Superhyperfine coupling from the imine nitrogens is observed in the g_2 branch (A_N ~ 15 G). These data are consistent with a distorted square-pyramidal geometry about copper with an unpaired electron in the $d_{x^2-y^2}$ orbital.

In contrast, the unbridged parent complex clearly displays a more rhombic spectrum at 77 K with Cu hyperfine coupling observed for both g_1 and g_3 branches; A_3 = 120 G and A_1 = 75 G. As for the bridged complexes, superhyperfine splitting of ~15 G is observed in the g_2 branch. The geometry of the unbridged

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[10] TEXSAN-TEXRAY Structure Analysis Package. Molecular Structure Corp. 1985.

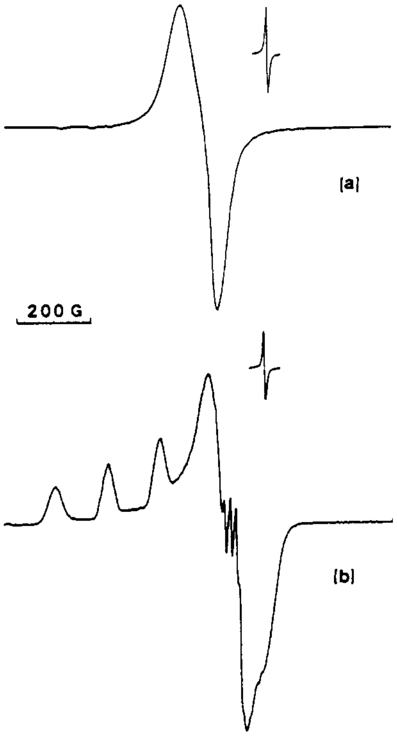

Figure 2. Isotropic (a) and anisotropic (b) ESR spectra in 1:1 benzene/toluene for [Cu{Me_2(C3)Me_2malMeDPT}].

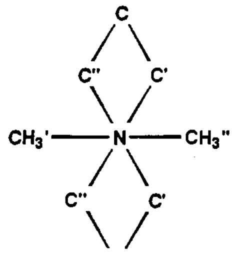

Figure 3. Schematic representation of the disorder in the MeDPT bridging group.

complex in solution appears to more nearly approximate a TBP than is the case with the bridged complexes, an inference that is consistent with their solid-state structures; vide infra.

Description of the Structures. Metal complexes of the Schiff base ligands comprised of the 2:1 condensation products of 2,4-pentanedione derivatives with dipropyltriamine species have been known for several years.[5] However, to our knowledge, the complexes reported herein are the first to be structurally characterized by single-crystal X-ray diffraction techniques. Superficially, the three complexes are structurally very similar, but a detailed analysis of the coordination sphere geometries presents significant differences in their solid-state structures. This is apparent in the following shape-determining angles analysis for the three structures.

Unbridged Complex. The unbridged complex consists of discrete copper–ligand molecules. The ligand binds in a pentadentate manner with the copper center chelated to the nitrogen and oxygen atoms of the two β-keto imine moieties and also to the nitrogen of the methyldipropylamine (MeDPT) group. The copper atom and the MeDPT nitrogen atom are located on the 2-fold axis; thus, only half of the complex is independently determined. The MeDPT bridging group is disordered with respect to the carbon atoms directly bound to the nitrogen. This disorder is shown schematically in Figure 3 and is constrained by symmetry to have a 50% occupancy factor for each carbon atom. (This sort of disorder is also seen in the various substituted salicylal/DPT complexes.[11-13]) The planes comprised of the β-keto imine moieties are tipped up from the MeDPT bridge, and the pairs of nitrogen and of oxygen chelating atoms are coordinated to the metal in a trans configuration. Figure 4 presents an ORTEP view of this complex with the atomic numbering scheme.

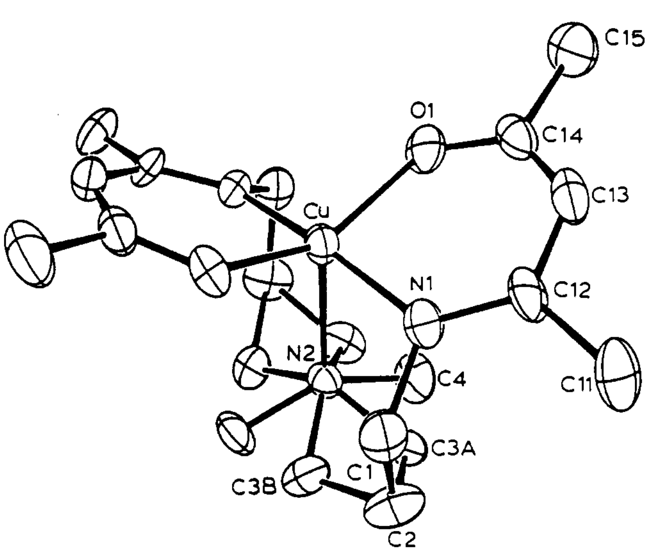

Figure 4. ORTEP drawing and atomic numbering scheme for [Cu($Me_2H_2Me_2$malMeDPT)].

The C6-Bridged Structure. The (C6) complex is monomeric, and its central copper atom is five-coordinate. As found for the parent complex, the β-keto imine groups are coordinated in a trans geometry. This compound exhibits the same sort of disorder about the nitrogen atom of the MeDPT, but unlike the unbridged structure, the two geometries are not equally populated. The structure refined with an occupany factor of 60% for the major component and 40% for the minor species.

Figure 5 presents three ORTEP views of this complex. The pocket created by the C6 bridge and the atomic numbering scheme are shown in Figure 5a. In Figure 5b, the molecule is rotated 90° relative to that of Figure 5a, while, in Figure 5c, the molecule is viewed down the axis of the copper–MeDPT nitrogen bond. For clarity, all three views show only the major component of the MeDPT linkage.

The C6 bridge between the γ carbons of the β-keto imine creates a hydrophobic pocket above the metal center. The distance between the copper atom and the hydrogen on C63 (the closest vertical approach) is 7.0 Å. The width of the cavity is 5.1 Å, which is the distance between O5 and O6 and also between the hydrogens on C18 and C38. Inspection of Figure 5b,c shows that the bridge is puckered and the orientations relative to the β-keto imine chelates are not symmetrical. On one side, the benzoyl riser nearly bisects the plane of the chelate ring (dihedral angle of 103°), but on the other side, the plane of the phenyl ring is slanted at a dihedral angle of 72° relative to the "N_2O_2 plane". Also, in the latter case, the carbonyl oxygen is twisted relative to the plane of the benzene riser at a torsion angle of ~35°. The folding of the polymethylene chain and the asymmetry of the bridge may be necessitated by crystal packing forces, rather than ligand geometrical constraints or electronic considerations. If this were indeed the case, a more symmetrical bridge orientation might be expected for solution species.

The C3-Bridged Structure. As with the unbridged and (C6) structures, the (C3) complex is also monomeric and the central copper atom is five-coordinate. This complex also exhibits an analogous disorder about the MeDPT nitrogen atom, but a ratio of 65% to 35% is observed for the major and minor components, respectively. Further, this complex exhibits a disorder involving two of the atoms of the polymethylene bridge; one fragment folds into the cavity toward the metal center, while the other fragment

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(11) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 808.

(12) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

(13) Di Vaira, M.; Orioli, P. L.; Sacconi, L. *Inorg. Chem.* **1971**, *10*, 553.

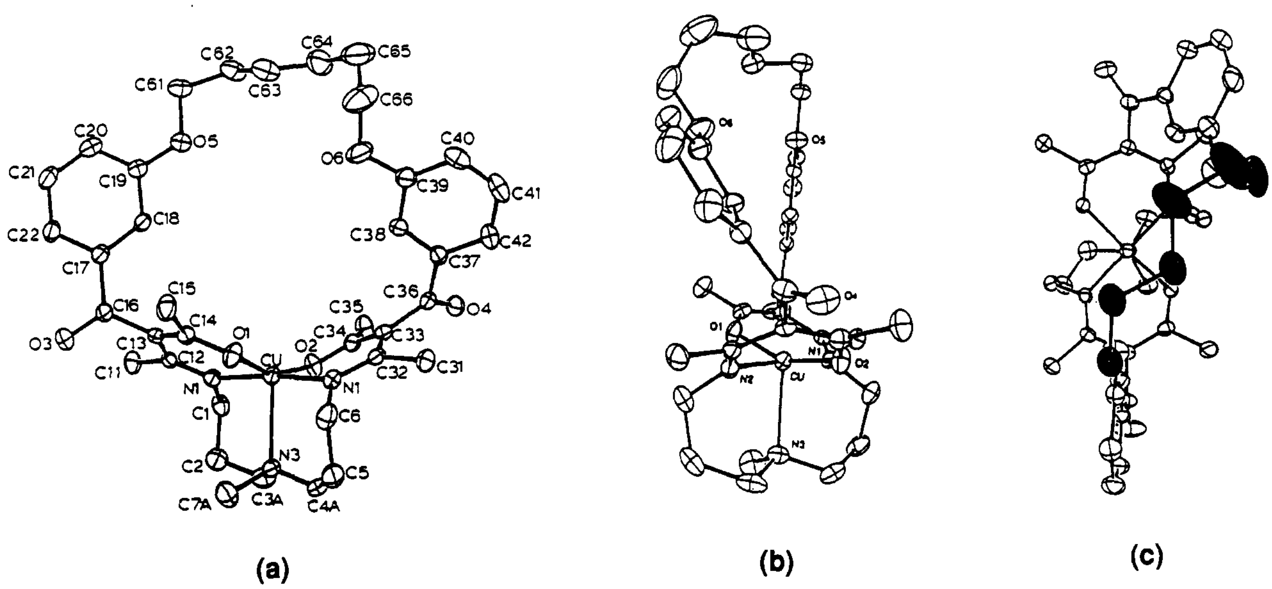

Figure 5. (a) ORTEP drawing and atomic numbering scheme for [Cu{Me$_2$(C6)Me$_2$malMeDPT}]. The disorder in the MeDPT unit is omitted for clarity. (b) ORTEP drawing of [Cu{Me$_2$(C6)Me$_2$malMeDPT}] rotated 90° relative to (a). (c) View of the same molecule down the copper–MeDPT nitrogen bond.

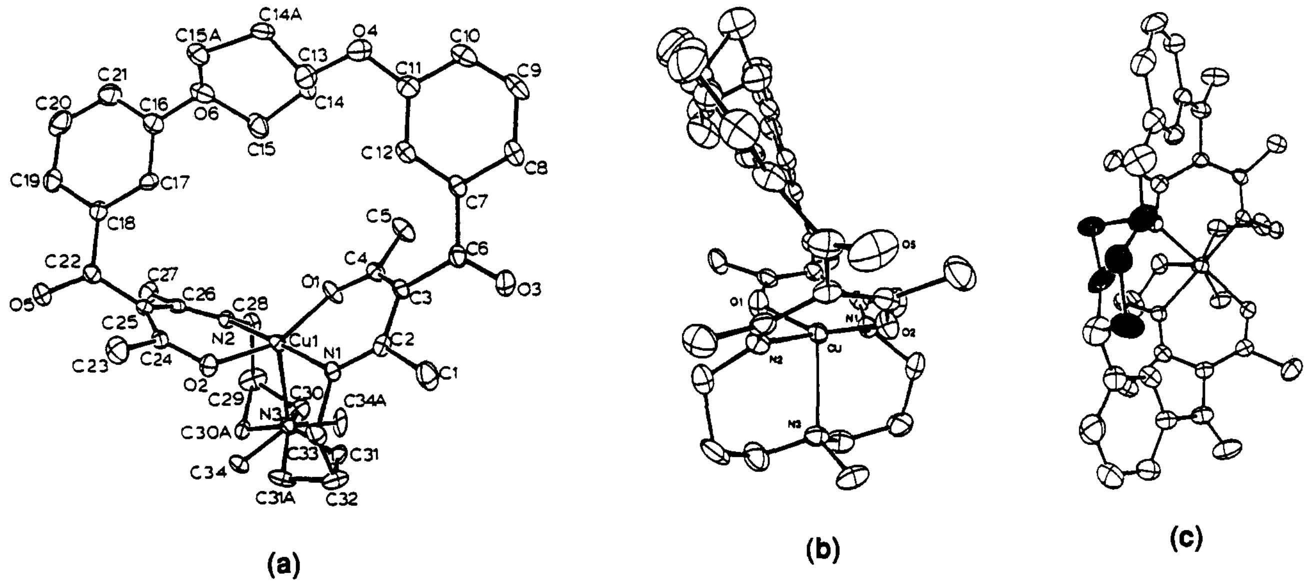

Figure 6. (a) ORTEP drawing and atomic numbering scheme for [Cu{Me$_2$(C3)Me$_2$malMeDPT}]. Both disorders are shown. (b) ORTEP drawing of [Cu{Me$_2$(C3)Me$_2$malMeDPT}] rotated 90° relative to (a). (c) View of the same molecule down the copper–MeDPT nitrogen bond.

rises above benzoyl risers, expanding the cavity. The disordered fragments adopt a chain conformation relative to each other and the nondisordered connecting carbon and oxygen atoms. Both fragments contribute equally to the structure. This is depicted in Figure 6. Figure 6a shows the cavity created by the C3 bridge as well as the atomic numbering scheme. As expected, the cavity dimensions are significantly contracted from that of the (C6) complex. The cavity height differs for the two different conformations presented by the bridge disorder. The smaller vertical dimension of the cavity is the distance between the copper center and the hydrogen on C15, 4.25 Å, while in the more open conformation the cavity height is 5.05 Å, the distance between copper and C15A. The cavity width is not affected by the disorder in the bridge; the distance between the hydrogen atoms on carbon 12 and carbon 17 is 4.645 Å. Close contacts are also observed between these hydrogens and the copper atom. The distances from the copper atom to H12 and H17 are 4.520 and 3.986 Å, respectively.

In both the (C3) and (C6) structures, the bridges are tilted relative to the copper–MeDPT nitrogen bond. This is clearly shown for the (C3) complex in Figure 6b, which is rotated 90° relative to Figure 6a. While the geometry of the C3 bridge is more symmetrically oriented relative to the β-keto imine rings, the bridge does not span directly over the metal center, as is shown in Figure 6c, a view taken down the copper–MeDPT nitrogen bond axis. The planes of the benzoyl groups rise at dihedral angles of 59.7 and 68.2° relative to the planes of their respective β-keto imine moieties. The dihedral angles between the two benzene risers is 18.1°. The carbonyl oxygens, O3 and O5, are rotated away from the plane of the benzene rings, as was seen on the asymmetrical side of the (C6) structure. They are displaced 0.287 and 0.600 Å, respectively, from the best least-squares plane of their respective benzene rings.

Coordination Geometry and Shape-Determining Angle Analysis. The coordination sphere bond distances and angles for the unbridged, the (C6), and the (C3) structures are presented in Table VI. All other bond distances and angles associated with the ligand carbon atoms are as expected and are available in the supplementary material.

For the unbridged and (C3) structures, the metal–ligand bond lengths for the chelating nitrogen and oxygen atoms of the β-keto imine moiety are essentially equivalent. This is also true for the copper–nitrogen and one of the copper–oxygen bond lengths of the (C6) complex. In the latter case, however, the Cu–O1 distance

Table III. Positional Parameters for [Cu{Me_2(C6)Me_2malMeDPT}]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	0.60389 (5)	0.32802 (4)	0.34854 (4)	H5	0.6218	0.1581	0.6176
O1	0.7989 (2)	0.3504 (2)	0.4114 (2)	H6	0.6211	0.0652	0.5294
O2	0.4398 (3)	0.3644 (2)	0.3355 (2)	H7	0.7585	0.1354	0.6416
O3	0.9805 (4)	0.1693 (2)	0.6527 (3)	H8	1.0463	0.3787	0.4817
O4	0.3476 (3)	0.6458 (2)	0.2640 (2)	H9	1.0845	0.3472	0.5936
O5	1.0414 (3)	0.6080 (2)	0.8959 (2)	H10	1.0598	0.4567	0.5893
O6	0.9278 (3)	0.8159 (2)	0.6090 (2)	H11	0.9324	0.4463	0.7219
N1	0.5941 (3)	0.2283 (2)	0.4353 (3)	H12	1.2144	0.5484	1.0668
N2	0.6103 (3)	0.4176 (2)	0.2515 (2)	H13	1.2601	0.3845	1.0442
N3	0.4822 (3)	0.1744 (2)	0.1747 (3)	H14	1.1431	0.2528	0.8651
C1	0.4514 (4)	0.1610 (3)	0.3882 (4)	H15	0.5738	0.5213	0.1005
C2	0.4021 (4)	0.0681 (3)	0.2803 (4)	H16	0.5232	0.6060	0.1512
C3A	0.3630 (8)	0.1098 (6)	0.1769 (7)	H17	0.6787	0.6161	0.2129
C3B	0.487 (1)	0.0822 (7)	0.2082 (8)	H18	0.2343	0.4764	0.2987
C4B	0.550 (1)	0.1849 (8)	0.1067 (9)	H19	0.3545	0.5408	0.4238
C4A	0.438 (1)	0.2108 (6)	0.0775 (6)	H20	0.2867	0.4181	0.3905
C5	0.5614 (5)	0.2861 (4)	0.0725 (4)	H21	0.7096	0.6681	0.4730
C6	0.6690 (4)	0.3787 (4)	0.1813 (4)	H22	0.8929	0.9817	0.5284
C7B	0.333 (1)	0.173 (1)	0.102 (1)	H23	0.6962	0.9786	0.3708
C7A	0.573 (1)	0.1057 (6)	0.1728 (8)	H24	0.5007	0.8232	0.2605
C11	0.6727 (4)	0.1374 (3)	0.5825 (4)	H25	1.0955	0.6735	1.0614
C12	0.6969 (4)	0.2136 (3)	0.5197 (3)	H26	1.2107	0.7164	1.0350
C13	0.8385 (4)	0.2687 (3)	0.5584 (3)	H27	0.9572	0.7578	0.9357
C14	0.8796 (4)	0.3309 (3)	0.5018 (3)	H28	1.0882	0.8416	1.0441
C15	1.0304 (4)	0.3803 (3)	0.5436 (4)	H29	1.1929	0.8713	0.9369
C16	0.9505 (4)	0.2513 (3)	0.6604 (3)	H30	1.0780	0.7751	0.8302
C17	1.0261 (4)	0.3377 (3)	0.7759 (3)	H31	0.9215	0.8650	0.8021
C18	1.0007 (4)	0.4348 (3)	0.7882 (3)	H32	1.0283	0.9585	0.9151
C19	1.0731 (4)	0.5150 (3)	0.8955 (3)	H33	0.9962	1.0084	0.7504
C20	1.1669 (4)	0.4953 (4)	0.9914 (3)	H34	1.1493	1.0173	0.8285
C21	1.1930 (4)	0.3983 (4)	0.9786 (3)	H35	1.1303	0.8745	0.7059
C22	1.1245 (4)	0.3196 (3)	0.8728 (3)	H36	1.0662	0.9463	0.6338
C31	0.5849 (4)	0.5642 (3)	0.1682 (3)	H21A	0.4719	0.0371	0.2882
C32	0.5649 (4)	0.4992 (3)	0.2425 (3)	H22A	0.3228	0.0136	0.2668
C33	0.4832 (3)	0.5262 (3)	0.2929 (3)	H31A	0.3063	0.0500	0.1066
C34	0.4173 (4)	0.4527 (3)	0.3274 (3)	H32A	0.3045	0.1538	0.1790
C35	0.3125 (4)	0.4731 (3)	0.3594 (4)	H41A	0.3799	0.1512	0.0073
C36	0.4603 (4)	0.6324 (3)	0.2993 (3)	H42A	0.3758	0.2532	0.0807
C37	0.5870 (4)	0.7304 (3)	0.3593 (3)	H51A	0.6065	0.2398	0.0516
C38	0.7094 (4)	0.7324 (3)	0.4525 (3)	H52A	0.5216	0.3157	0.0094
C39	0.8194 (4)	0.8254 (3)	0.5175 (3)	H21B	0.4046	0.0039	0.3008
C40	0.8126 (5)	0.9154 (3)	0.4834 (4)	H22B	0.3071	0.0593	0.2265
C41	0.6959 (5)	0.9133 (3)	0.3887 (5)	H31B	0.5850	0.0894	0.2607
C42	0.5810 (4)	0.8222 (3)	0.3251 (4)	H32B	0.4532	0.0197	0.1437
C61	1.1111 (4)	0.6946 (3)	1.0027 (3)	H41B	0.6462	0.1858	0.1528
C62	1.0579 (5)	0.7861 (3)	0.9750 (4)	H42B	0.5072	0.1244	0.0384
C63	1.0946 (5)	0.8325 (4)	0.8950 (4)	H51B	0.5875	0.2797	0.0131
C64	1.0182 (7)	0.9074 (4)	0.8490 (4)	H52B	0.4729	0.2968	0.0394
C65	1.0608 (7)	0.9667 (5)	0.7803 (5)	H71B	0.3292	0.2319	0.0818
C66	1.0526 (5)	0.9026 (5)	0.6803 (5)	H72B	0.2785	0.1887	0.1419
H1	0.4445	0.1332	0.4456	H71A	0.6670	0.1640	0.1873
H2	0.3916	0.2035	0.3673	H72A	0.6089	0.0683	0.2389
H3	0.7051	0.4363	0.1607	H73B	0.2756	0.1140	0.0235
H4	0.7430	0.3542	0.2264	H73A	0.5071	0.0213	0.1032

of 1.930 (3) Å is anomalously short.

The copper–MeDPT nitrogen bond length in all three compounds is significantly longer than the copper–nitrogen distance for the β-keto imine moiety and is probably a result of Jahn–Teller effects. While elongation was anticipated, the deviations observed between the structures was not expected. The 2.326 (5) Å distance in the (C3) complex is significantly shorter than the 2.415 (3) and 2.389 (3) Å distances of the (C6) and unbridged structures, respectively, and could be a result of the relatively lesser flexibility inherent in the shorter polymethylene bridge. Since the ability of a cobalt center to bind dioxygen is directly related to the electron density at the metal,[14] the shorter axial bond length of the (C3) complex could indicate a significantly greater dioxygen affinity for the corresponding cobalt complex as compared with the analogous unbridged and (C6) species. The observed structural differences for the copper complexes, however, may not be seen for other metal species. For a series of divalent copper, nickel, and zinc complexes with a similar ligand, Freyberg and co-workers observed that elongation of the axial metal–nitrogen bond occurred only for the copper complex and, thus, was not a steric requirment of the ligand.[12]

Superficially, the geometry about the copper centers for all three complexes appears identical. With the exception of the O1–Cu–O2 and N1–Cu–N2 bond angles, little variation between the three structures is observed for the various metal-ligating atom bond angles presented in Table VI. The coordination geometry of the copper atom in all three structures is intermediate between that of a trigonal bipyramid (TBP) and a square pyramid (SP). This description is, however, rather imprecise, and therefore, a more detailed analysis based on certain shape determining angles has been performed.

A given polyhedron may be quantitatively described by the dihedral angles between its various planes. Muetterties and Guggenberger[6] have refined a method whereby complexes of intermediate geometry are compared with idealized polyhedra. With five-coordinate geometry, the molecule would ideally have D_{3h} (TBP) or C_{4v} (SP) symmetry. These polyhedra are sketched

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[14] Carter, M. J.; Rillema, D. P.; Basolo, F. *J. Am. Chem. Soc.* **1974**, *96*, 392.

Table IV. Positional Parameters for [Cu{Me_2(C3)Me_2malMeDPT}]

atom	*x*	*y*	*z*
Cu1	0.45247 (8)	0.15971 (2)	0.04738 (4)
O1	0.6142 (5)	0.1450 (1)	−0.0097 (2)
O2	0.2542 (4)	0.1616 (1)	0.0695 (2)
O3	0.6889 (6)	0.2246 (2)	−0.2066 (3)
O4	0.4818 (6)	0.0740 (2)	−0.2938 (3)
O5	0.0223 (6)	0.0676 (1)	0.1425 (3)
O6	0.3636 (6)	0.0110 (2)	−0.1040 (3)
N1	0.4438 (5)	0.2055 (1)	−1.0115 (3)
N2	0.4663 (6)	0.1147 (1)	0.1091 (3)
N3	0.5398 (6)	0.1941 (1)	0.1466 (3)
C1	0.4831 (8)	0.2501 (2)	−0.1128 (4)
C2	0.5035 (6)	0.2130 (2)	−0.0750 (4)
C3	0.5921 (6)	0.1861 (2)	−0.1119 (3)
C4	0.6488 (7)	0.1564 (2)	−0.0738 (3)
C5	0.7710 (7)	0.1351 (2)	−0.1034 (4)
C6	0.6427 (7)	0.1942 (2)	−0.1885 (4)
C7	0.6334 (7)	0.1648 (2)	−0.2479 (4)
C8	0.7053 (7)	0.1706 (2)	−0.3143 (4)
C9	0.6990 (8)	0.1445 (3)	−0.3714 (4)
C10	0.6231 (8)	0.1135 (2)	−0.3616 (4)
C11	0.5518 (8)	0.1068 (2)	−0.2968 (4)
C12	0.5564 (7)	0.1328 (2)	−0.2403 (3)
C13	0.4193 (9)	0.0629 (2)	−0.2287 (5)
C14	0.531 (2)	0.0472 (4)	−0.1842 (9)
C14A	0.364 (2)	0.0253 (4)	−0.2324 (7)
C15A	0.275 (2)	0.0117 (4)	−0.1669 (8)
C15	0.469 (2)	0.0423 (5)	−0.1081 (9)
C16	0.2824 (8)	0.0074 (2)	−0.0404 (4)
C17	0.2560 (7)	0.0373 (2)	0.0042 (4)
C18	0.1693 (7)	0.0338 (2)	0.0649 (3)
C19	0.1131 (8)	−0.0007 (2)	0.0810 (4)
C20	0.144 (1)	−0.0308 (2)	0.0366 (6)
C21	0.228 (1)	−0.0270 (2)	−0.0242 (5)
C22	0.1305 (8)	0.0671 (2)	0.1092 (4)
C23	0.0282 (7)	0.1409 (2)	0.0720 (4)
C24	0.1792 (7)	0.1333 (2)	0.0835 (3)
C25	0.2254 (7)	0.0989 (2)	0.1063 (3)
C26	0.3682 (8)	0.0926 (2)	0.1275 (3)
C27	0.3942 (8)	0.0596 (2)	0.1785 (4)
C28	0.6044 (7)	0.1098 (2)	0.1401 (4)
C29	0.631 (1)	0.1358 (2)	0.2062 (4)
C30A	0.526 (2)	0.1711 (5)	0.218 (1)
C30	0.663 (1)	0.1769 (4)	0.1751 (7)
C31	0.583 (1)	0.2310 (3)	0.1175 (7)
C31A	0.453 (3)	0.2271 (6)	0.161 (1)
C32	0.463 (1)	0.2542 (2)	0.0865 (4)
C33	0.3707 (7)	0.2345 (2)	0.0304 (4)
C34A	0.668 (2)	0.2041 (8)	0.132 (1)
C34	0.434 (1)	0.1987 (4)	0.2066 (6)
H1A	0.5199	0.2694	−0.0812
H1B	0.5320	0.2505	−0.1586
H1C	0.3882	0.2538	−0.1222
H5A	0.7492	0.1094	−0.1064
H5B	0.7941	0.1441	−0.1518
H5C	0.8469	0.1385	−0.0708
H8	0.7579	0.1926	−0.3206
H9	0.7481	0.1484	−0.4165
H10	0.6189	0.0957	−0.4008
H12	0.5060	0.1287	−0.1956
H13	0.3637	0.0810	−0.2044
H14AB	0.4390	0.0087	−0.2366
H14AA	0.3090	0.0238	−0.2762
H14B	0.6071	0.0636	−0.1828
H14A	0.5593	0.0238	−0.2041
H15AA	0.2011	0.0283	−0.1585
H15AB	0.2405	−0.0125	−0.1768
H15B	0.5401	0.0373	−0.0735
H15A	0.4247	0.0651	−0.0947
H17	0.2972	0.0607	−0.0066
H19	0.0530	−0.0035	0.1224
H20	0.1075	−0.0546	0.0488
H21	0.2474	−0.0478	−0.0551
H23A	−0.0001	0.1606	0.1040
H23B	0.0126	0.1478	0.0214
H23C	−0.0229	0.1191	0.0832
H27A	0.3111	0.0463	0.1858
H27B	0.4605	0.0437	0.1566
H27C	0.4270	0.0682	0.2255
H28B	0.6696	0.1147	0.1020
H28A	0.6139	0.0848	0.1565
H29	0.6817	0.1267	0.2476
H32	0.4629	0.2805	0.0910
H33B	0.2967	0.2234	0.0566
H33A	0.3363	0.2524	−0.0039

Table V. ESR Spectra Parameters for the Copper(II) Complexes[a]

complex	g_0	g_1	g_2	g_3	A_3, G
[Cu($Me_2H_2Me_2$malMeDPT)]	2.112	2.028	2.065[b]	2.243	120
[Cu{Me_2(C3)Me_2malMeDPT}]	2.108	2.015[b]	2.064	2.245	143
[Cu{Me_2(C6)Me_2malMeDPT}]	2.113	2.029[b]	2.064	2.246	141

[a] $\sim 5 \times 10^{-3}$ M in 1:1 v/v benzene/toluene solution. [b] Calculated from the measured tensors using the relationship $3g_{iso} = (g_1 + g_2 + g_3)$.

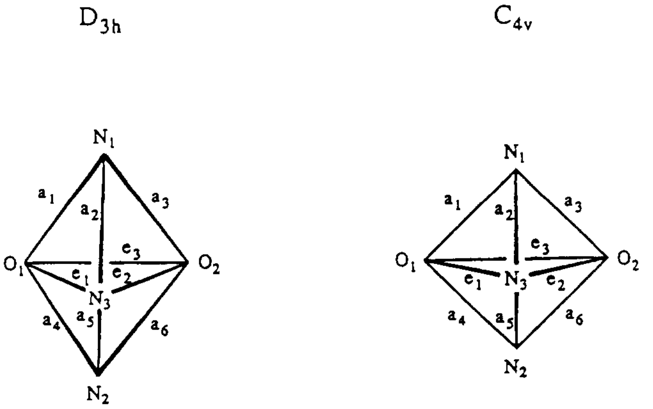

Figure 7. Idealized polyhedra for five-coordinate geometries and their shape-determining angles a_n and e_n, adapted from Muetterties and Guggenberger.[6]

Table VI.

Bond Distances (Å) for the Three Structures[a]

	unbridged	(C6)	(C3)
Cu-O1	1.963 (2)	1.930 (3)	1.953 (3)
Cu-O2	1.963 (2)	1.969 (3)	1.976 (4)
Cu-N1	1.962 (2)	1.962 (3)	1.954 (2)
Cu-N2	1.962 (2)	1.960 (3)	1.962 (2)
Cu-N3	2.389 (3)	2.415 (3)	2.326 (5)

Bond Angles (deg) for the Three Structures[a]

	unbridged	(C6)	(C3)
O1-Cu-N1	92.0 (1)	90.7 (1)	88.9 (2)
O1-Cu-N2	90.4 (1)	89.3 (1)	90.9 (2)
O1-Cu-N3	106.9 (1)	107.4 (1)	104.4 (2)
O2-Cu-N1	90.4 (1)	94.3 (1)	92.1 (2)
O2-Cu-N2	92.0 (1)	87.6 (1)	89.0 (2)
O2-Cu-N3	106.9 (1)	96.5 (1)	100.8 (2)
O1-Cu-O2	146.3 (1)	155.7 (1)	154.9 (2)
N1-Cu-N2	171.9 (1)	175.3 (1)	177.8 (2)
N1-Cu-N3	86.0 (1)	87.8 (1)	88.9 (2)
N2-Cu-N3	86.0 (1)	87.7 (1)	89.0 (2)

[a] For comparison purposes, the MeDPT nitrogen of the unbridged structure has been relabeled N3, while O2 and N2 are the atoms symmetry-related to O1 and N2, respectively.

below with their shape-determining dihedral angles defined (*a*1–*a*6 and *e*1–*e*3) (Figure 7). The vertices of the TBP and SP polyhedra are labeled with the ligating atoms of the pentadente ligands. With the N1–Cu–N2 angle near 180°, these atoms occupy the "axial" positions of the distorted trigonal bipyramid, while the two oxygen atoms and the nitrogen from the MeDPT group occupy the "equatorial" plane. Clearly, if the molecule were square planar, then N1 and N2 and the two oxygen atoms would be coplanar, with the MeDPT nitrogen occupying the apical position. In this

Table VII. Shape-Determining Angles (deg) for the Copper(II) Complexes

	D_{3h}	unbridged	(C6)	(C3)	C_{4v}
e_1	53.1	63.3	63.2	65.9	75.7
e_2	53.1	63.3	71.6	69.1	75.7
e_3	53.1	39.7	27.7	26.7	0.0
a_1	101.5	104.2	112.3	110.8	119.8
a_2	101.5	91.9	89.0	86.3	75.7
a_3	101.5	104.8	105.1	108.1	119.8
a_4	101.5	104.8	111.3	110.2	119.8
a_5	101.5	91.9	85.4	85.9	75.7
a_6	101.5	104.2	106.0	109.0	119.8
$e_{1,2}$[a]	53.1	63.3	67.4	67.5	75.7
e_3	53.1	39.7	27.7	26.7	0.0
$a_{2,5}$[a]	101.5	91.0	87.2	86.1	75.7
a_n[b]	101.5	104.5	108.7	109.5	119.8

[a] Average values. [b] Average of a_1, a_3, a_4, and a_6.

case, the dihedral angle between the planes defined by N1, O1, and O2 and N2, O1, and O2 should be zero.

Table VII presents the dihedral angles for the three structures, as well as those of the idealized D_{3h} and C_{4v} polyhedra. For a TBP configuration, the dihedral angles associated with the equatorial plane, e_1, e_2, and e_3, are equivalent (53.1°). For SP geometry, two of the equatorial angles are equivalent, 75.7°, while the third equals 0.0°, as previously illustrated. Similarly, the axial dihedral angles for TBP geometry are all 101.5°, but for SP, two sets of angles are observed. Those pertaining to the angle between the square base are 119.8°, while those relating to the planes joined at the apex are 75.7°.

For all three structures, the dihedral angles of the various planes are clearly between the extremes set by the idealized cases. Also, the geometries of the (C6) and (C3) structures, on the average, are indistinguishable. This is shown in the averaged values. The e_3 value of $\sim 27°$ is midway between the 53.3 and the 0.0° values required for the TBP and SP geometries, respectively. Similarly, the various a angles are also close to the median values for the two limiting cases. Inspection of the individual angles for both structures, however, indicates that the geometry about the (C3) complex is more regular, as was seen in comparison of the copper–nitrogen and copper–oxygen bond lengths with the β-keto imine moieties.

The parent complex again distinguishes itself; while intermediate between the two idealized geometries, it has a geometry more like D_{3h} than C_{4v}. This difference in geometry was also observed in the ESR experiments, where the unbridged complex gave rise to a spectrum qualitatively different from those of the nearly identical (C6) and (C3) spectra.

Conclusions

The superstructures added to the simple pentadentate Schiff base copper(II) complexes at the γ positions of the β-keto imines have been structurally characterized. Because of the variety of bridging groups that are available for these syntheses, the facile demetalation of the copper complexes, and the subsequent ease of insertion of cobalt(II), a molecular design for control of the dioxygen-carrying ability should be achievable with these systems. X-ray structural determinations of the copper complexes confirm that hydrophobic pockets of varying size can be created above the metal center, a strategy that has been highly successful with the cyclidene complexes of cobalt(II).[3,15] Moreover, the presence of the bridging group has a substantial effect on the metal coordination geometry, forcing the ligand to adopt a more planar environment than that found for the corresponding unbridged complex. From the method of Muetterties and Guggenberger,[6] the geometry of the bridged complexes is calculated to reside equally distant from both SP and TBP coordination geometries. The unbridged structure more nearly approximates the TBP configuration. These geometrical variations were also inferred for solution species on the basis of ESR spectroscopy.

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Supplementary Material Available: Tables S1–S9, listing interatomic distances and angles and non-hydrogen thermal parameters for all three structures (16 pages); Tables S10–S12, listing observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

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