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Crystal and Molecular Structure of Bis(dimethylglyoximato)(imidazole)copper(II)

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Received November 27, 1979

The solid-state structure of bis(dimethylglyoximato)(imidazole)copper(II) has been determined by X-ray crystallographic analysis. The compound crystallizes in the orthorhombic space group *Pbca* with unit cell dimensions $a = 8.468$ (1), $b = 28.647$ (4), and $c = 12.413$ (1) Å. The structure was refined by full-matrix least-squares techniques to $R = 0.043$ and $R_w = 0.065$ against the full set of 3108 F^2 values. The coordination geometry of the copper atom is that of a distorted square pyramid with the four dimethylglyoximato nitrogens forming the basal plane at an average distance of 1.955 (3) Å. The copper atom is displaced 0.353 (1) Å from this plane toward the axial imidazole group. The Cu–N(imidazole) bond length is 2.141 (1) Å. Two asymmetric O–H···O hydrogen bonds of lengths 2.524 (2) and 2.598 (2) Å link the dimethylglyoximato moieties. An intermolecular (imidazole) N–H···O hydrogen bond is formed to the oxygen atom of the longer intramolecular hydrogen bond.

Introduction

Recent studies have emphasized the importance of the copper–imidazole(histidine) bond in both "blue" copper proteins and "nonblue" copper proteins.[2-4] Specific ligands and coordination geometries for the metal sites have been proposed[5] by comparison of the protein spectra with those of a series of model complexes. The study of these complexes suggested a distorted square-pyramidal configuration at the copper sites in galactose oxidase, in oxyhemocyanin, and in the magnetically coupled ion pairs believed to constitute type III copper. An axially coordinated thiolate ion was proposed for the square-pyramidal copper in galactose oxidase and an axial imidazole for oxyhemocyanin. Indeed, a five-coordinate copper(I) hemocyanin model containing two imidazole ligands does reversibly bind oxygen[6] although no structural data are yet available.

Additional studies demonstrate that Cu(II) bound to four square-planar N donors exhibits a high affinity for an axial ligand in both the oxidized and reduced state, with a reduction potential strongly dependent on the nature of the fifth ligand.[7] Although the square-pyramidal configuration is unusual for Cu(I), recent NMR evidence demonstrates that the axially bound imidazole in [*N*-(mercaptoacetyl)glycyl-DL-histidyl-DL-histidine]copper(II) retains the square-pyramidal coordination after reduction.[8]

These results suggest that an axial imidazole nitrogen may have a specific function in maintaining the coordination geometry during the electron-transfer process. Imidazole is a good σ donor for Cu(II), and as a π acceptor, it is also capable of stabilizing Cu(I).[9,10]

The recent structural study of the galactose oxidase model (1,8-diamino-3,6-dithiaoctane)(1-methylimidazole)copper(II) perchlorate,[11] has confirmed the proposed[5] distorted square-pyramidal geometry with an axially coordinated thioether.

Table I

Data Collection	
diffractometer	Enraf-Nonius CAD4
radiatn	Cu Kα graphite monochromated ($\lambda = 1.540\ 51$ Å)
attenuator	nickel foil, $I_0/I_{att} = 15.55$
linear abs coeff	16.35 cm^{-1} (Cu Kα)
2θ range	$0° \leqslant 2\theta \leqslant 150°$
no. of reflctns	8689, 3108 unique
scattering factors	ref 15
anomalous dispersion	ref 16
refinement	full-matrix least-squares against F^2's
R_{F^2}	0.043
R_{wF^2}	0.065[a]
Programs Used	
abs correctn and averaging	BNLABS/AVSORT[17]
refinement	FLINUS[17]
fourier transforms	JIMDAP[17]
dist, angles, planes	FREDFUN[17]
diagrams	ORTEP II[18]

[a] Where $w = 1/\sigma^2$ and $\sigma^2 = \sigma_c^2 + (0.015F^2)^2 + [0.015(F^2 - F^2/A)]$.

Bis(dimethylglyoximato)(imidazole)copper(II), which was synthesized as part of a series of monomeric Lewis base adducts of (dimethylglyoximato)copper(II), presents the first structurally characterized example of a square-pyramidal Cu(II) complex having an axial imidazole.

The dimethylglyoxime complexes are of general interest since they have frequently been used as models for the biologically important porphyrin systems, most notably vitamin B_{12} and hemoglobin. They are also capable of forming intramolecular hydrogen bonds which have been the subject of extensive study.[12]

Experimental Section

Bis(dimethylglyoximato)(imidazole)copper(II) was prepared by reacting 0.0681 g (10^{-3} mol) of imidazole in 10 mL of methanol with a solution of bis(dimethylglyoximato)copper(II) (0.2938 g, 10^{-3} mol) in 100 mL of methanol. The resulting solution was stirred for 12 h at room temperature and filtered, and the volume of the filtrate was reduced until solid material began to form. The product was filtered off, washed with methanol and petroleum ether, and dried in vacuum. Recrystallization from methanol gave dark red-brown needles (mp 189–190 °C). Anal. Calcd for $C_{11}H_{18}N_6O_4Cu$: C, 36.51; H, 5.01; N, 23.23. Found: C, 36.46; H, 5.20; N, 23.29 (Galbraith Laboratories, Knoxville, Tenn). The complex was further characterized as described elsewhere.[13]

A well-formed crystal of approximate dimensions 0.6 × 0.1 × 0.2 mm was mounted with its long dimension approximately parallel to the fiber axis and examined by precession photography by using Mo

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Table II. Fractional Atomic Coordinates and Anisotropic Thermal Motion Coefficients for One Molecule[a] and Fractional Coordinates, Isotropic Thermal Motion Terms, Bonding Atoms, and Bond Distances for the Hydrogen Atoms

ATOM	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
CU1	2456(3)	12832(1)	9026(2)	293(1)	363(1)	341(1)	3(1)	-31(1)	12(1)
O1	-13455(17)	18921(5)	-6739(12)	481(8)	511(8)	530(8)	24(6)	-126(6)	140(7)
O2	17905(18)	15965(6)	28747(12)	561(8)	763(10)	438(7)	-96(7)	-166(7)	-27(8)
O3	-20175(14)	10086(4)	-7597(9)	302(6)	521(7)	328(6)	-11(5)	-65(5)	59(5)
O4	11711(16)	7365(6)	27727(11)	451(7)	642(9)	371(7)	18(6)	-143(6)	93(6)
N1	-4991(17)	18697(5)	2698(12)	307(7)	405(7)	425(8)	30(6)	-0(6)	39(7)
N2	10523(17)	17296(6)	19648(12)	378(8)	505(9)	396(8)	-35(6)	-19(6)	-58(7)
N3	-12310(15)	8756(5)	1367(11)	262(6)	406(7)	294(6)	13(5)	-0(5)	17(6)
N4	2936(16)	7477(5)	18601(11)	320(7)	477(8)	300(7)	51(6)	-23(6)	30(6)
N5	23041(16)	11960(5)	-785(12)	265(7)	400(7)	389(7)	2(5)	19(6)	-3(6)
N6	47003(20)	10578(5)	-6779(14)	281(8)	445(8)	578(10)	28(6)	51(7)	23(8)
C1	-4172(37)	27236(8)	3127(29)	749(18)	369(10)	869(19)	46(11)	100(15)	26(12)
C2	-592(22)	22466(6)	7324(17)	367(10)	387(8)	565(11)	5(7)	137(8)	-19(8)
C3	8240(22)	21673(6)	17528(17)	399(9)	487(10)	477(10)	-75(8)	97(8)	-122(9)
C4	13646(38)	25532(10)	24646(24)	820(18)	616(14)	675(16)	-251(14)	175(13)	-245(14)
C5	-25305(27)	1095(7)	1220(19)	472(11)	442(11)	503(13)	-65(9)	6(9)	-58(9)
C6	-14377(19)	4671(6)	5620(13)	299(8)	379(8)	342(8)	13(6)	59(6)	-7(7)
C7	-5236(19)	3907(6)	15625(14)	305(8)	396(8)	351(8)	38(6)	55(7)	32(7)
C8	-5653(31)	-582(8)	21666(22)	634(14)	515(11)	574(13)	-38(11)	-17(11)	173(11)
C9	23063(23)	11975(7)	-11782(16)	348(9)	525(10)	394(9)	2(8)	-62(8)	-4(8)
C10	37793(21)	11094(7)	1933(16)	310(9)	467(9)	458(10)	2(7)	-52(7)	41(9)
C11	37652(24)	11126(8)	-15600(17)	456(11)	526(10)	444(10)	-9(9)	94(8)	-36(9)

atom	x	y	z	B, Å^2	atom bonded to	dist, Å	atom	x	y	z	B, Å^2	atom bonded to	dist, Å
H_1	−0.127 (4)	0.271 (1)	−0.040 (3)	8.8 (9)	C_1	1.15 (4)	H_{10}	−0.015 (5)	−0.031 (2)	0.185 (4)	13 (1)	C_8	0.89 (5)
H_2	0.055 (4)	0.289 (1)	0.012 (3)	7.6 (7)	C_1	0.97 (3)	H_{11}	−0.012 (5)	−0.003 (1)	0.294 (4)	10 (1)	C_8	1.04 (5)
H_3	−0.059 (3)	0.288 (1)	0.077 (2)	5.6 (7)	C_1	0.74 (3)	H_{12}	−0.161 (4)	−0.018 (1)	0.226 (3)	7.0 (7)	C_8	0.96 (3)
H_4	0.225 (5)	0.271 (1)	0.217 (4)	11 (1)	C_4	0.94 (4)	H_{13}	0.143 (3)	0.125 (1)	−0.151 (2)	5.5 (6)	C_9	0.86 (3)
H_5	0.153 (5)	0.240 (2)	0.322 (4)	12 (1)	C_4	1.04 (4)	H_{14}	0.422 (3)	0.108 (1)	0.089 (2)	4.9 (5)	C_{10}	0.95 (3)
H_6	0.054 (5)	0.271 (1)	0.275 (4)	11 (1)	C_4	0.90 (5)	H_{15}	0.419 (3)	0.109 (1)	−0.237 (2)	4.8 (5)	C_{11}	1.07 (3)
H_7	−0.277 (4)	0.013 (1)	−0.061 (3)	8.1 (8)	C_5	0.94 (3)	H_{16}	0.573 (4)	0.102 (1)	−0.070 (2)	6.2 (7)	N_6	0.88 (3)
H_8	−0.211 (4)	−0.017 (1)	0.006 (3)	8.6 (9)	C_5	0.88 (4)	H_{17}	−0.166 (3)	0.154 (1)	−0.086 (2)	7.6 (7)	O_1	1.07 (3)
H_9	−0.345 (4)	0.011 (1)	0.050 (3)	8.0 (8)	C_5	0.91 (4)	H_{18}	0.152 (4)	0.108 (1)	0.279 (3)	10 (1)	O_4	1.04 (4)

[a] Standard deviations in units of least significant figures are given in parentheses. The vibration factor has the form $T = [-2^2(h^2a^{*2}U_{11} + 2a^*b^*hkU_{12} + \ldots)]$. Atomic coordinates have been multiplied by 10^5 and thermal vibration parameters by 10^4.

Kα radiation. Orthorhombic diffraction symmetry with the systematic absence of $k = 2n + 1$ for $0kl$ reflections, $l = 2n + 1$ for $h0l$ reflections, and $h = 2n + 1$ for $hk0$ reflections was observed and the space group *Pbca* (No. 61) thereby deduced.[14]

The unit cell dimensions are $a = 8.468$ (1), $b = 28.647$ (4), and $c = 12.412$ (1) Å, and their standard deviations were obtained from a least-squares refinement against the setting angles of 25 reflections on an Enraf-Nonius CAD4 diffractometer using Cu Kα radiation. The calculated density of 1.596 g/cm^3 based on eight molecules per cell agree well with the experimental density of 1.595 g/cm^3 determined by its neutral bouyancy in pure carbon tetrachloride.

During the 9 days of data collection there was no significant variation in the intensities of three reflections monitored periodically. Some experimental details are given in Table I.

Solution and Refinement

The position of the copper atom was deduced from a three-dimensional vector map, and the remaining atoms were located in successive Fourier syntheses. Refinement of this model was carried out by full-matrix least-squares methods against all unique intensity data with one reflection removed because of unusually large discrepancy.

The nonhydrogen atoms were refined anisotropically, while isotropic thermal parameters were assigned to hydrogen atoms. In the final cycle, all parameter shifts were reduced to less than their nominal standard deviations.

The structure of the molecular complex is shown in Figure 1, and the final atomic parameters are given in Table II. Bond distances and angles are listed in Tables III and IV. The equations of some

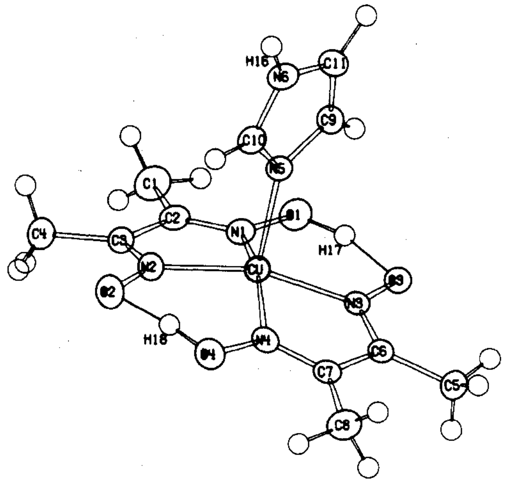

Figure 1. View of the molecular complex showing the intramolecular hydrogen bonds and the atomic nomenclature.

Table III. Bond Distances (Å)

Cu-N_1	1.960 (1)	N_2-C_3	1.297 (2)
Cu-N_2	1.960 (2)	N_3-C_6	1.296 (2)
Cu-N_3	1.958 (1)	N_4-C_7	1.289 (2)
Cu-N_4	1.942 (1)	C_1-C_2	1.494 (3)
Cu-N_5	2.141 (1)	C_2-C_3	1.488 (2)
N_1-O_1	1.375 (2)	C_3-C_4	1.488 (2)
N_2-O_2	1.346 (2)	C_5-C_6	1.485 (3)
N_3-O_3	1.352 (2)	C_6-C_7	1.480 (2)
N_4-O_4	1.355 (2)	C_7-C_8	1.490 (3)
N_1-C_2	1.279 (2)		
N_5-C_9[a]	1.365 (2)	N_6-C_{11}[a]	1.360 (3)
N_5-C_{10}[a]	1.318 (2)	C_9-C_{11}[a]	1.345 (3)
N_6-C_{10}[a]	1.341 (3)		

[a] Imidazole group.

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Table IV. Bond Angles (Deg)

N_1-Cu-N_3	96.42 (6)	C_4-C_3-N_2	123.6 (1)
N_1-Cu-N_2	79.73 (6)	O_2-N_2-C_3	116.3 (1)
N_2-Cu-N_4	95.57 (6)	O_2-N_2-Cu	122.8 (1)
N_4-Cu-N_3	80.72 (6)	O_3-N_3-Cu	123.1 (1)
N_1-Cu-N_5	97.72 (5)	O_3-N_3-C_6	121.6 (1)
N_2-Cu-N_5	100.07 (5)	C_5-C_6-N_3	123.9 (2)
N_3-Cu-N_5	100.05 (5)	C_5-C_6-C_7	122.2 (2)
N_4-Cu-N_5	103.81 (5)	C_8-C_7-C_6	122.5 (2)
O_1-N_1-Cu	123.3 (1)	C_8-C_7-N_4	123.6 (2)
O_1-N_1-C_2	119.7 (1)	O_4-N_4-C_7	121.0 (1)
C_1-C_2-N_1	123.9 (2)	O_4-N_4-Cu	122.8 (1)
C_1-C_2-C_3	122.6 (2)	$O_2 \cdots H_{18}$-O_4	172 (3)
C_4-C_3-C_2	123.1 (2)	O_1-$H_{17} \cdots O_3$	162 (3)
C_9-N_5-C_{10}[a]	104.8 (1)	N_6-C_{11}-C_9[a]	105.8 (2)
N_5-C_{10}-N_6[a]	111.4 (2)	C_{11}-C_9-N_5[a]	110.7 (2)
C_{10}-N_6-C_{11}[a]	107.3 (1)		

[a] Imidazole group.

Table V. Least-Squares Planes

A. Displacements in Å

atom/ plane	I	II	III	IV
Cu	0.353[a]	−0.088[a]		0.013
N_1	−0.012[b]			−0.036
N_2	0.012			
N_3	0.010		−0.033	
N_4	−0.010		0.004	
N_5		0.000		
N_6		0.001		
C_1				−0.029
C_2				−0.017
C_3				−0.010
C_4				0.045
C_5			0.046	
C_6			−0.017	
C_7			−0.016	
C_8			−0.027	
C_9		0.000		
C_{10}		−0.001		
C_{11}		−0.001		
O_1				0.029
O_2				0.007
O_3			0.009	
O_4			0.034	

B. Equations for Fractional Coordinates

I $7.022x - 4.493y - 6.659z - 1.358 = 0$

II $1.636x + 28.125y + 0.0398z + 3.740 = 0$

III $-6.504x + 0.869y + 6.701z - 1.790 = 0$

IV $-7.273x - 0.115y + 6.356z - 0.500 = 0$

[a] Atom excluded from calculation of plane. Esd for Cu displacement is 0.001 Å. [b] Standard deviations for displacements of N, C, and O atoms average 0.002 Å.

mean planes and the displacements of some atoms from them are given in Table V.

A listing of observed and calculated structure factors is available as supplementary material.

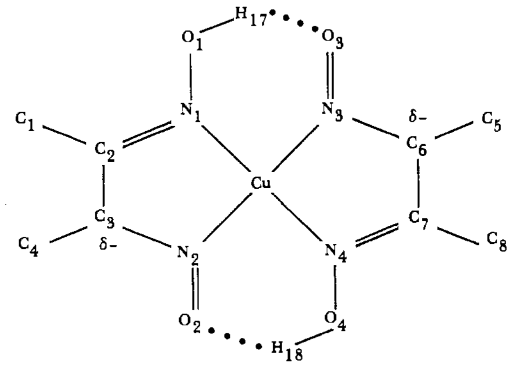
Results and Discussion

The imidazole adduct of bis(dimethylglyoximato)copper(II) crystallizes as discrete, neutral monomers with a five-coordinate square-pyramidal configuration about the copper atom which is displaced 0.353 (1) Å from the best plane of the four dimethylglyoxime nitrogen atoms. The relationship between this displacement toward the axial ligand and the position of the d–d absorption band has recently been demonstrated by Addison and co-workers.[7] The planes of the two chelating ligands intersect the basal plane at angles of 11.3 (1) and 9.5 (1)°, being bent back from the fifth coordination site. The axial imidazole ring is perpendicular to the basal plane and approximately parallel to the bisector of the two O···O bridges. The equations of the relevant least-squares planes are given in Table V.

The four dimethylglyoxime copper–nitrogen bond lengths (average value = 1.955 (3) Å) are consistent with those in other structural reports,[19] while the fifth bond is elongated to 2.141 (1) Å. This is considerably shorter than the Cu–N(axial) bond lengths in similar square-pyramidal Cu(II) complexes. The quinoline adduct of bis(acetylacetonato)copper(II) has a Cu–N axial bond length of 2.36 (1) Å,[20] while bis(*N*-phenylsalicylaldimato)(pyridine)copper(II) has a Cu–N(axial) bond length of 2.31 Å.[21] Lingafelter and co-workers also reported a longer Cu–N axial bond distance of 2.357 (4) Å in bis[2,2′-iminobis(acetamidoxime)]copper(II) chloride.[22] The smaller displacement of the copper atom from the coordination plane (~0.2 Å in each) correlates with the longer apical bond length.[23] Two structural studies of complexes in which the copper site is intermediate between trigonal-bipyramidal and square-pyramidal geometries do show shorter Cu–N(axial) bond lengths of 2.148 (17)[24] and 2.16 (3) Å.[25]

The Cu–N(imidazole) distance is longer than the value 2.011 (5) Å recently reported[11] for the equatorial methyl imidazole coordinated to square-pyramidal Cu(II) but much shorter than the axial value of 2.593 (3) Å observed in the distorted octahedral $[Cu(Im)_6]^{2+}$ ion.[26] Previously published equatorial Cu–N(imidazole) bond lengths range from 1.913 (7) to 2.049 (2) Å,[26–30] although a value of 2.145 (5) Å was found for the equatorial dimethylimidazole of the trigonal-bipyramidal complex dichlorotris(1,2-dimethylimidazole)copper(II).[31]

The geometry of the dimethylglyoxime moiety should indicate the extent of cyclic delocalization in the planar, five-membered chelate ring as well as the contribution of resonance forms such as structure II.



II

Vaciago and Zambonelli[19] concluded that this canonical form does make a significant contribution to the structure of the bis(dimethylglyoximato)copper(II) dimer. Their data do

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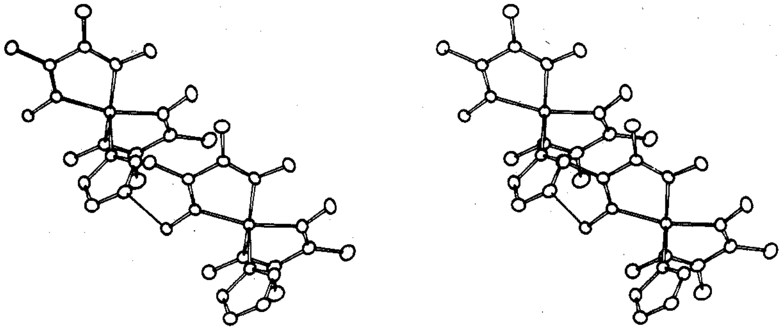

Figure 2. Two molecules related by unit translation along *a* linked together by the intermolecular hydrogen bond.

not support extensive delocalization, and our results are in reasonably good agreement.

The four carbon–nitrogen bond lengths average 1.290 (2) Å with a significant difference between C_2–N_1 (1.279 (2) Å) and C_3–N_2 (1.297 (2) Å) and possibly significant difference between C_6–N_3 (1.296 (2) Å) and C_7–N_4 (1.289 (2) Å). The reduction of double-bond character for C_3–N_2 and C_6–N_3 is evident by comparison with the normal C–N double-bond length (1.265 Å) calculated from the atomic radii.

The N_1–O_1 bond (1.375 (2) Å) is significantly longer than the other three, while N_2–O_2 (1.346 (2) Å) is the shortest, although it falls within the statistical range of N_3–O_3 (1.352 (2) Å). This dimethylglyoxime group therefore can be approximately represented by structure II. The greater similarity of the two C–N bonds in the second dimethylglyoxime as well as the shorter C_6–C_7 bond (1.480 (2) Å vs. 1.488 (2) Å for C_2–C_3) suggests more delocalization in this ligand. The average values of the two different N–O bond types represented in structure II are 1.365 (10) and 1.349 (3) Å.

The N_2–O_2 bond shows the largest percentage of double-bond character when compared with the value 1.397 (4) Å reported for uncoordinated glyoxime.[32] The longer distance observed for N_3–O_3 may be due to an additional intermolecular hydrogen bond from O_3 to the N–H group of a neighboring imidazole.

The C_2–C_3 and C_6–C_7 bond lengths are appropriate for single-bonded sp^2 carbon atoms. The trigonal hybridization is further supported by the tabulated bond angles and the planarity of the dimethylglyoxime groups. The average of the four C–CH_3 bonds, 1.489 (3) Å, is appreciably shorter than the mean published value of 1.510 Å,[33] an effect which we ascribe to the comparatively large thermal motion of the methyl groups.

The intramolecular hydrogen bonds bridging the dimethylglyoxime ligands are asymmetric with each hydrogen covalently bonded to one oxygen and hydrogen bonded to the other. This arrangment occurs in several metal glyoxime complexes[12,34] and was postulated for bis(dimethylglyoximato)copper(II) although the second bridging hydrogen atom was not located.[19]

The dimensions of the hydrogen bonds are as follows: O_1–H_{17} = 1.07 (3) Å; $H_{17}\cdots O_3$ = 1.56 (3) Å, with the angle O–H···O = 162 (3)°; O_4–H_{18} = 1.04 (4) Å; $H_{18}\cdots O_2$ = 1.50 (4) Å, with the angle O–H···O = 172 (3)°.

The O···O distances are 2.524 (2) and 2.598 (2) Å for O_2–O_4 and O_1–O_3, respectively, the longer distance being associated with the intermolecular hydrogen bond between O_3 and the N_6–H_{16} group of the imidazole in a symmetry-related molecule. The $H_{16}\cdots O_3$ contact (1.91 Å) links the monomeric units in a chainlike structure in the lattice. This is illustrated in the packing diagram shown in Figure 2.

The geometry of the imidazole group is in good agreement with that found for imidazole at −150 °C[35] and in similar metal complexes.[26–30] The copper atom is displaced 0.088 (1) Å, from the best plane of the imidazole group. The N_5–C_9 single-bond length, 1.365 (2) Å, is somewhat shorter than that observed for most Cu(II)-coordinated imidazole groups measured with comparable precision. The average value of 10 such N–C imidazole bond lengths is 1.374 (5) Å[26,27,30] compared with 1.378 Å for uncoordinated imidazole and 1.382 (9) Å for $Fe(im)_2(DMG)_2$. The axially coordinated imiadazole of octahedral $[Cu(im)_6](NO_3)_2$ has an N–C bond length of 1.378 (5) Å. However, in this case the metal is displaced 1.261 Å from the plane of the imidazole ring[26] inhibiting π interaction. The axial dimethylimidazole of trigonal-bipyramidal $CuCl_2(dimim)_3$ also shows a comparable N–C bond length of 1.381 (7) Å.[30]

Although axial imidazole groups have been shown to act as both σ and π donors[10] as well as π acceptors,[9] there is no unequivocal structural evidence to support a particular mode of bonding in a specific metalloprotein system. The electronic details of such interactions must be inferred from model systems since it is beyond the present capacity of macromolecular crystallography to provide parameters of the required precision. The Cu–N(axial) linkage reported here is unusually short, but the geometry of the coordinated imidazole is not indicative of any unusual electronic perturbations. We are, however, currently investigating the analogous Cu(I) complex, since any structural alterations which accompany reduction are clearly of relevance to the biochemistry of cuproproteins.

Acknowledgment. S.M.M. gratefully acknowledges the financial support provided by a Research Corp. Grant. Research was carried out, in part, at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. Bis(dimethylglyoximato)(imidazole)copper(II), 74868-87-4; bis(dimethylglyoximato)copper(II), 14221-10-4.

Supplementary Material Available: A listing of observed and calculated squared structure factors (17 pages). Ordering information is given on any current masthead page.

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