Crystal and Molecular Structure of the {2,6-Bis[1-(2-imidazol-4-ylethylimino)ethyl]pyridine}-zinc(II) and -copper(II) Cations: Five-co-ordinate Relatives of a Copper(I) Oxygen Carrier

By **James D. Korp** and **Ivan Bernal,*** Department of Chemistry, The University of Houston, Houston, Texas 77004 U.S.A.
Connie L. Merrill and **Lon J. Wilson,*** The Department of Chemistry, William Marsh Rice University, Houston, Texas 77001, U.S.A.

The crystal and molecular structures of the two title compounds are reported and discussed as they relate to the analogous copper(I) derivative which reacts reversibly with O_2 in solution under ambient conditions. The five-co-ordinate $[Cu^{II}(imep)][ClO_4]_2$ and $[Zn^{II}(imep)][ClO_4]_2$ complexes are isomorphous and isostructural, being derived from a single quinquedentate ligand {imep = 2,6-bis[1-(2-imidazol-4-ylethylimino)ethyl]pyridine} containing one pyridine nitrogen atom, two imine nitrogen atoms, and two imidazole nitrogen-donor atoms to give MN_5 primary co-ordination spheres. The co-ordination about Cu^{II} and Zn^{II} is best described as intermediate between an idealized trigonal bipyramid and a square pyramid, with a potential sixth site lying *trans* to the pyridine nitrogen-donor atom (and between the imidazole rings) where a small molecule like O_2 is most likely to bind in the copper(I) species. Crystal data for $[Cu^{II}(imep)][ClO_4]_2$: space group $C2/c$, $Z = 8$, $a = 19.065(9)$, $b = 11.370(4)$, $c = 23.802(12)$ Å, and $R = 0.043$ for 1 939 reflections. Crystal data for $[Zn^{II}(imep)][ClO_4]_2$: space group $C2/c$, $Z = 8$, $a = 19.414(8)$, $b = 11.313(4)$, $c = 24.012(6)$ Å, and $R = 0.051$ for 2 551 reflections.

We have recently reported that the title compound with M = Cu^{I} {$[Cu^{I}(imep)]^{+}$ in Figure 1} reacts reversibly with molecular oxygen under ambient conditions in solution.[1-3] If this reaction involves simple adduct formation of O_2 as a ligand, the $[Cu^{I}(imep)]^{+}$ cation is the first synthetic copper(I) oxygen carrier found to function in the solution state,† despite the large number of synthetic O_2 complexes now known for several other metals.[4]

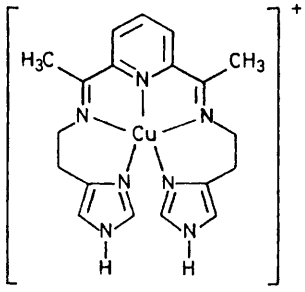

FIGURE 1 General structure of the $[Cu^{I}(imep)]^{+}$ cation

A special interest associated with $[Cu^{I}(imep)]^{+}$ as an oxygen carrier is its potential as a model compound for the bimetallated copper(I) active site of the naturally occurring haemocyanin proteins, and, like deoxyhaemocyanin, $[Cu^{I}(imep)]^{+}$ reacts reversibly with O_2 in a 2 : 1 (Cu : O_2) stoicheiometry giving an oxy-form which is essentially e.s.r. silent.[1-3]

An obvious advantage that model compounds offer over their more complex naturally occurring counterparts is the detailed structural information that can be gathered as an aid toward understanding structure–function–reactivity relationships. Thus, structural characterization of deoxy-$[Cu^{I}(imep)]^{+}$ and its oxy-form is of considerable interest and these results will be reported in subsequent work. In this paper we communicate the structural features associated with $[Cu^{II}(imep)][ClO_4]_2$ and with $[Zn^{II}(imep)][ClO_4]_2$, an isoelectronic analogue of the deoxy-copper(I) compound. Unlike the copper(I) compound, the zinc(II) and copper(II) species are unreactive toward O_2, allowing the crystals to be grown and handled under ambient conditions.

† A bimetallated copper(I) ' earmuff ' compound has been reported to reversibly bind O_2 in the solid state, J. E. Bulkowski, P. L. Burk, M. Ludmann, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1977, 498.

EXPERIMENTAL

Crystals of $[Zn^{II}(imep)][ClO_4]_2$ are pale yellow, while those of $[Cu^{II}(imep)][ClO_4]_2$ are dark green. Single crystals of each were mounted on an Enraf–Nonius CAD-4 automatic diffractometer using Mo-K_α radiation monochromatized by a dense graphite crystal, assumed to be ideally imperfect. Lattice constants and orientation matrices were obtained from least-squares fits of 25 automatically centred reflections distributed over reciprocal space. Final cell constants, as well as other pertinent data, are given in Table 1. The details of the data collections were similar, except as noted below. The Laue symmetry in both cases was determined to be $2/m$, and from the systematic absences noted, the space groups were both found to be $C2/c$.

Intensities were measured using the θ—2θ scan technique, with the scan rates depending on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every 2 h of exposure time as a check of electronic reliability and crystal stability, and showed no unusual trends during the course of the data collections. In each case, a unique quarter of the reciprocal sphere was collected, according to the limits in Table 1. In reducing the data, Lorentz and polarization factors were applied, but no corrections were made for absorption since the absorption coefficients were both small. An acceptance criterion of $I > 3\sigma(I)$ was employed in determining the reflections to be used in the least-squares refinements.

The structure of $[Zn^{II}(imep)][ClO_4]_2$ was solved first by use of the Patterson method to determine the location of the metal atom in the unit cell. Subsequent difference-

TABLE 1

Summary of data collection and processing parameters *

Formula	Zinc complex $C_{19}H_{23}Cl_2N_7O_8Zn$	Copper complex $C_{19}H_{23}Cl_2CuN_7O_8$
Space group	$C2/c$	$C2/c$
a/Å	19.414(8)	19.065(9)
b/Å	11.313(4)	11.370(4)
c/Å	24.012(6)	23.802(12)
β/°	108.50(3)	108.17(4)
U/Å^3	5 001	4 902
M	613.72	611.89
D_c/g cm^{-3}	1.63	1.66
μ/cm^{-1}	11.83	11.00
$F(000)$	312	311
Scan speed range/ ° min^{-1}	0.4—4.0	0.4—3.4
Total data collected	3 244	3 173
Data with $\|I\| > 3\sigma(I)$	2 551	1 939
Total variables	408	430
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.051	0.043
$R' = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}$	0.050	0.038

* The following parameters are the same for both complexes: monoclinic, $Z = 8$; data collection range, $4 < 2\theta < 45°$; scan width, $\Delta\theta = 1.10 + 0.35 \tan\theta$; maximum scan time, 300 s; and weights, $w = \sigma(|F|)^{-2}$.

Fourier syntheses revealed the positions of all the remaining atoms, including the hydrogens. The six methyl hydrogens behaved poorly and had to be fixed in the final cycles of refinement, which is why the zinc structure had fewer variables than the copper. Since the two compounds appeared to be isomorphous and isostructural, the atomic co-ordinates from the zinc refinement were used as the starting positions in the copper refinement, and they showed only slight deviations at the conclusion, when all shift-to-error ratios were less than 0.1. The final agreement factors for both structures are given in Table 1. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree–Fock wavefunctions;[5] for hydrogen, those of Stewart *et al.*[6] were used. All calculations were made with the SHELX-76 series of programs by G. M. Sheldrick.[7] In the zinc refinement, there were high correlations between the scale factor and the zinc thermal parameters, but this was not observed in the copper refinement. Final positional parameters are listed in Tables 2 and 3 (a zero entry for estimated standard deviation indicates the parameter was held constant). Thermal parameters and structure factor tables are deposited in Supplementary Publication No. SUP 23064 (31 pp.).* Bond lengths, angles, least-squares planes, and torsion angles based on these positions are given in Tables 4—7. The numbering scheme employed is shown in Figure 2. The hydrogens have numbers corresponding to the atoms to which they are bonded.

RESULTS AND DISCUSSION

As can be seen from Table 4, the carbon–carbon and carbon–nitrogen distances of homologous bonds in the two structural refinements are all within *ca.* 4σ of each other, which indicates no discernable perturbation in the basic framework of the quinquedentate (imep) ligand due to the change in the central metal atom. Similarly, no evidence exists for any alteration of the resonance patterns in the ring systems of the ligands. The pyridyl ring is quite similar to those found in other structures with chelated metals,[8,9] as well as to gaseous pyridine.[10] The only significant difference is the C–N–C angle, which for the present structures averages 122.6°, but is usually much smaller, *ca.* 117°.[10] This deviation is most likely due to the strain at the points of connection to the pyridine ring [C(11), C(15)] of the atoms involved in the five-membered rings containing the metal atom. The tendency would obviously be to open up the C–N–C angle, as can be seen in Figure 2. A similar effect has been seen previously.[11]

The imidazole rings also agree quite well with previously reported results,[12,13] including the shortening in the attachment to the ethane bridges at C(5)–C(6) and C(21)–C(22).[12] They are all quite planar, as can be seen from Table 6, indicating no unusual strain involved in the rotation necessary to properly approach the metal atom. Several structures are known in which the same ligand framework from N(8) to N(19) is found, making them tridentate,[11,14] as well as one which is also quinquedentate,[15] and our results compare favourably with those found previously. There is very nearly a two-fold (C_2) axis of symmetry running through the centre of the ligand

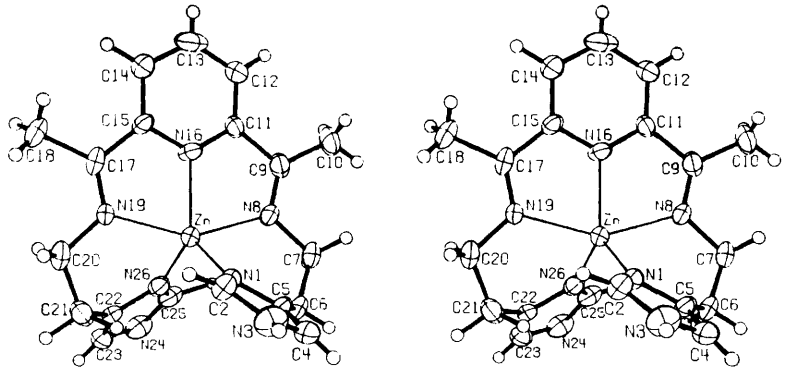

FIGURE 2 Stereoscopic view of the atom labelling scheme used for both refinements. The thermal ellipsoids are 50% equiprobability envelopes, with hydrogens shown as spheres of arbitrary diameter. Note the distortion of the co-ordination about the metal atom from either a square-pyramidal or trigonal-bipyramidal configuration

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 2

Atomic co-ordinates for $[Zn^{II}(imep)][ClO_4]_2$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Zn	0.099 07(4)	−0.060 07(7)	0.897 91(3)
Cl(1)	0.219 9(1)	0.386 2(2)	0.830 6(1)
Cl(2)	0.446 6(1)	0.040 3(2)	0.865 4(1)
O(1)	0.144 3(3)	0.439 4(5)	0.831 0(3)
O(2)	0.251 5(3)	0.469 1(4)	0.808 1(2)
O(3)	0.251 3(3)	0.356 2(6)	0.890 0(3)
O(4)	0.198 7(3)	0.279 1(5)	0.798 5(3)
O(5)	0.434 1(4)	−0.060 7(6)	0.890 1(4)
O(6)	0.335 0(3)	0.116 5(5)	0.845 3(3)
O(7)	0.472 0(4)	0.014 9(5)	0.816 5(3)
O(8)	0.501 4(4)	0.113 1(8)	0.903 2(3)
N(1)	0.122 1(3)	−0.164 5(5)	0.839 6(2)
C(2)	0.028 6(3)	−0.269 1(7)	0.817 2(3)
N(3)	0.134 9(3)	−0.307 1(5)	0.782 2(2)
C(4)	0.185 4(4)	−0.221 8(7)	0.782 8(3)
C(5)	0.173 4(3)	−0.134 0(6)	0.818 3(3)
C(6)	0.216 3(3)	−0.019 5(6)	0.831 9(3)
C(7)	0.267 7(3)	−0.001 0(6)	0.896 4(3)
N(8)	0.215 3(3)	−0.031 4(5)	0.934 3(2)
C(9)	0.245 6(3)	−0.062 5(6)	0.967 7(3)
C(10)	0.325 6(3)	−0.058 7(7)	1.021 9(3)
C(11)	0.194 4(3)	−0.108 4(6)	1.019 1(3)
C(12)	0.213 7(3)	−0.147 8(6)	1.075 1(3)
C(13)	0.159 6(5)	−0.192 6(6)	1.094 4(3)
C(14)	0.088 2(4)	−0.198 6(6)	1.059 5(3)
C(15)	0.071 4(3)	−0.154 4(5)	1.003 3(3)
N(16)	0.125 0(3)	−0.114 0(4)	0.984 4(2)
C(17)	−0.001 6(3)	−0.149 7(5)	0.958 6(3)
C(18)	−0.066 3(3)	−0.185 5(7)	0.977 4(3)
N(19)	−0.004 4(2)	−0.107 2(4)	0.908 6(2)
C(20)	−0.073 3(3)	−0.087 5(6)	0.863 1(3)
C(21)	−0.063 0(3)	−0.023 5(6)	0.810 3(3)
C(22)	−0.019 9(3)	0.088 7(6)	0.824 2(2)
C(23)	−0.037 9(5)	0.199 7(7)	0.807 2(3)
N(24)	0.021 0(4)	0.268 5(7)	0.530 6(3)
C(25)	0.073 9(4)	0.200 8(6)	0.862 9(3)
N(26)	0.052 7(3)	0.089 1(5)	0.860 0(2)
H(2)	0.058(2)	−0.309(4)	0.821(2)
H(3)	0.129 (3)	−0.377(5)	0.766(2)
H(4)	0.207(3)	−0.228(5)	0.759(2)
H(6A)	0.187(3)	0.040(6)	0.819(3)
H(6B)	0.250(2)	−0.014(4)	0.813(2)
H(7B)	0.302(3)	−0.068(5)	0.909(2)
H(7B)	0.265(3)	0.079(5)	0.898(3)
H(10A)	0.337(0)	−0.146(0)	1.029(0)
H(10B)	0.356(0)	−0.046(0)	1.003(0)
H(10C)	0.338(0)	0.011(0)	1.050(0)
H(12)	0.253(2)	−0.144(4)	1.099(2)
H(13)	0.163(2)	−0.224(4)	1.121(2)
H(14)	0.049(3)	−0.224(5)	1.075(2)
H(13A)	−0.086(0)	−0.118(0)	0.999(0)
H(13B)	−0.099(0)	−0.218(0)	0.945(0)
H(18C)	−0.049(0)	−0.250(0)	1.000(0)
H(20A)	−0.097(2)	−0.045(4)	0.875(2)
H(20B)	−0.095(2)	−0.152(4)	0.853(2)
H(21A)	−0.027(3)	−0.073(5)	0.791(2)
H(21B)	−0.116(3)	−0.009(4)	0.783(2)
H(23)	−0.076(3)	0.225(5)	0.783(2)
H(24)	0.022(4)	0.338(6)	0.831(3)
H(25)	0.144(4)	0.221(6)	0.886(3)

TABLE 3

Atomic co-ordinates for $[Cu^{II}(imep)][ClO_4]_2$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Cu	0.098 68(4)	−0.048 02(8)	0.907 75(4)
Cl(1)	0.211 3(1)	0.398 1(2)	0.831 9(1)
Cl(2)	0.442 6(1)	0.047 7(2)	0.864 4(1)
O(1)	0.143 6(2)	0.451 1(5)	0.832 2(2)
O(2)	0.253 1(3)	0.480 5(5)	0.809 7(2)
O(3)	0.252 0(3)	0.368 2(6)	0.891 7(2)
O(4)	0.197 1(3)	0.293 3(5)	0.798 6(2)
O(5)	0.424 2(4)	−0.051 4(6)	0.887 0(4)
O(6)	0.382 7(3)	0.128 6(6)	0.846 3(3)

TABLE 3 (*continued*)

Atom	*x/a*	*y/b*	*z/c*
O(7)	0.467 9(3)	0.021 8(5)	0.814 6(3)
O(8)	0.501 0(4)	0.108 1(8)	0.903 8(3)
N(1)	0.118 1(3)	−0.152 6(5)	0.842 4(2)
C(2)	0.096 1(4)	−0.257 4(7)	0.820 7(3)
N(3)	0.131 8(3)	−0.293 6(5)	0.783 9(3)
C(4)	0.181 9(4)	−0.205 9(7)	0.782 9(3)
C(5)	0.173 1(3)	−0.119 9(6)	0.819 2(3)
C(6)	0.208 0(4)	−0.002 2(7)	0.831 9(3)
C(7)	0.251 8(3)	0.021 0(6)	0.896 7(3)
N(8)	0.211 2(3)	−0.018 7(5)	0.936 8(2)
C(9)	0.245 4(3)	−0.055 6(6)	0.988 9(3)
C(10)	0.326 8(4)	−0.050 6(7)	1.018 7(3)
C(11)	0.197 1(3)	−0.110 6(6)	1.019 4(3)
C(12)	0.216 8(4)	−0.157 2(7)	1.076 1(3)
C(13)	0.162 5(4)	−0.208 5(7)	1.095 9(3)
C(14)	0.087 3(4)	−0.211 1(6)	1.060 2(3)
C(15)	0.072 5(3)	−0.162 0(6)	1 005 2(3)
N(16)	0.125 5(3)	−0.112 9(5)	0.986 2(2)
C(17)	−0.001 6(4)	−0.149 4(6)	0.960 5(3)
C(18)	−0.069 1(4)	−0.192 2(7)	0.974 6(3)
N(19)	−0.002 0(3)	−0.099 0(5)	−0.911 9(2)
C(20)	−0.071 9(3)	−0.076 6(6)	0.865 0(3)
C(21)	−0.059 5(3)	−0.012 5(7)	0.813 3(3)
C(22)	−0.016 9(4)	0.098 8(7)	0.826 9(3)
C(23)	−0.035 1(4)	0.209 9(7)	0.809 0(3)
N(24)	0.024 7(4)	0.276 4(5)	0.833 6(3)
C(25)	0.078 1(4)	0.208 1(7)	0.867 3(3)
N(26)	0.055 6(3)	0.098 9(5)	0.865 4(2)
H(2)	0.069(2)	−0.296(4)	0.836(2)
H(3)	0.136(4)	−0.372(7)	0.761(3)
H(4)	0.208(3)	−0.211(5)	0.763(2)
H(6A)	0.167(3)	0.065(5)	0.813(2)
H(6B)	0.234(2)	0.008(4)	0.811(2)
H(7A)	0.290(2)	−0.022(4)	0.906(2)
H(7B)	0.261(3)	0.111(6)	0.903(3)
H(10A)	0.345(3)	0.021(6)	1.007(3)
H(10B)	0.341(4)	0.024(4)	1.057(3)
H(10C)	0.337(3)	−0.106(5)	1.028(2)
H(12)	0.271(3)	−0.144(5)	1.105(2)
H(13)	0.179(4)	−0.244(6)	1.135(3)
H(14)	0.046(3)	−0.263(5)	1.080(2)
H(18A)	−0.057(5)	−0.272(8)	1.003(4)
H(18B)	−0.117(4)	−0.207(7)	0.926(3)
H(18C)	−0.075(4)	−0.177(8)	1.015(4)
H(20A)	−0.101(2)	−0.041(4)	0.876(2)
H(20B)	−0.100(3)	−0.152(6)	0.847(2)
H(21A)	−0.045(2)	−0.056(4)	0.785(2)
H(21B)	−0.104(2)	−0.003(4)	0.786(2)
H(23)	−0.073(2)	0.239(4)	0.789(2)
H(24)	0.032(3)	0.343(4)	0.833(2)
H(25)	0.124(2)	0.246(4)	0.893(2)

TABLE 4

Bond lengths (Å) for $[M^{II}(imep)][ClO_4]_2$

	M = Zn	M = Cu
Cl(1)–O(1)	1.428(6)	1.426(5)
Cl(1)–O(2)	1.437(6)	1.433(6)
Cl(1)–O(3)	1.436(6)	1.434(6)
Cl(1)–O(4)	1.416(6)	1.411(6)
Cl(2)–O(5)	1.344(8)	1.341(8)
Cl(2)–O(6)	1.425(6)	1.424(6)
Cl(2)–O(7)	1.434(8)	1.444(7)
Cl(2)–O(8)	1.422(7)	1.393(7)
M–N(1)	1.988(5)	2.081(6)
M–N(8)	2.180(5)	2.066(5)
M–N(16)	2.067(5)	1.923(5)
M–N(19)	2.171(5)	2.036(6)
M–N(26)	1.992(5)	1.992(5)
N(1)–C(2)	1.319(9)	1.314(9)
N(1)–C(5)	1.390(9)	1.379(9)
C(2)–N(3)	1.329(10)	1.331(11)
N(3)–C(4)	1.372(10)	1.385(10)
C(4)–C(5)	1.344(10)	1.349(11)
C(5)–C(6)	1.474(9)	1.484(10)
C(6)–C(7)	1.529(8)	1.529(9)
C(7)–N(8)	1.487(10)	1.473(10)
N(8)–C(9)	1.276(8)	1.280(8)

TABLE 4 (*continued*)

	M = Zn	M = Cu
C(9)–C(10)	1.511(8)	1.492(9)
C(9)–C(11)	1.516(10)	1.478(10)
C(11)–C(12)	1.352(9)	1.388(10)
C(11)–N(16)	1.342(7)	1.346(7)
C(12)–C(13)	1.372(12)	1.392(12)
C(13)–C(14)	1.376(10)	1.422(9)
C(14)–C(15)	1.376(9)	1.369(10)
C(15)–N(16)	1.341(9)	1.350(9)
C(15)–C(17)	1.483(8)	1.487(8)
C(17)–C(18)	1.519(11)	1.509(11)
C(17)–N(19)	1.276(9)	1.289(10)
N(19)–C(20)	1.451(7)	1.470(7)
C(20)–C(21)	1.527(10)	1.511(11)
C(21)–C(22)	1.499(9)	1.483(10)
C(22)–C(23)	1.332(10)	1.344(11)
C(22)–N(26)	1.399(7)	1.400(8)
C(23)–N(24)	1.350(10)	1.340(9)
N(24)–C(25)	1.318(10)	1.332(9)
C(25)–N(26)	1.325(9)	1.309(10)
H *	0.70–1.32	0.67–1.23

* The range of bonding distances for all hydrogens in each structure is given.

TABLE 5

Bond angles (°) for $[M^{II}(imep)][ClO_4]_2$

	M = Zn	M = Cu
N(1)–M–N(16)	119.6(2)	116.8(2)
N(1)–M–N(26)	110.6(2)	104.0(2)
N(16)–M–N(26)	129.8(2)	139.2(2)
N(8)–M–N(16)	75.5(2)	78.6(2)
N(8)–M–N(19)	150.8(2)	157.9(2)
N(16)–M–N(19)	75.4(2)	79.3(2)
M–N(1)–C(2)	133.9(5)	134.6(5)
M–N(1)–C(5)	119.4(4)	118.6(4)
C(2)–N(1)–C(5)	106.4(6)	106.0(6)
N(1)–C(2)–N(3)	111.3(6)	111.9(7)
C(2)–N(3)–C(4)	106.7(6)	106.6(6)
N(3)–C(4)–C(5)	108.1(7)	106.7(7)
C(4)–C(5)–C(6)	130.3(7)	130.4(7)
C(4)–C(5)–N(1)	107.5(6)	108.8(6)
N(1)–C(5)–C(6)	122.1(6)	120.7(6)
C(5)–C(6)–C(7)	115.3(6)	115.5(6)
C(6)–C(7)–N(8)	109.7(5)	111.6(5)
C(7)–N(8)–C(9)	120.9(5)	121.2(5)
M–N(8)–C(7)	121.7(3)	122.2(4)
M–N(8)–C(9)	116.3(5)	115.7(5)
N(8)–C(9)–C(10)	126.6(7)	125.9(7)
N(8)–C(9)–C(11)	115.8(5)	114.1(5)
C(10)–C(9)–C(11)	117.6(5)	119.9(6)
C(9)–C(11)–C(12)	126.1(5)	128.1(5)
C(9)–C(11)–N(16)	113.2(5)	113.1(5)
C(12)–C(11)–N(16)	120.6(6)	118.8(6)
C(11)–C(12)–C(13)	117.2(6)	118.9(6)
C(12)–C(13)–C(14)	122.9(6)	121.6(6)
C(13)–C(14)–C(15)	117.3(7)	115.5(7)
C(14)–C(15)–N(16)	119.2(5)	122.5(5)
C(14)–C(15)–C(17)	126.7(7)	126.1(7)
N(16)–C(15)–C(17)	114.0(6)	111.4(6)
C(11)–N(16)–C(15)	122.6(5)	122.6(5)
M–N(16)–C(11)	119.1(5)	118.5(5)
M–N(16)–C(15)	118.3(4)	118.9(4)
C(15)–C(17)–C(18)	117.7(6)	119.7(6)
C(15)–C(17)–N(19)	116.2(6)	115.1(6)
C(18)–C(17)–N(19)	125.9(5)	125.2(5)
C(17)–N(19)–C(20)	121.4(6)	120.6(6)
M–N(19)–C(17)	116.0(4)	115.3(4)
M–N(19)–C(20)	122.6(4)	124.0(5)
N(19)–C(20)–C(21)	111.6(5)	111.5(5)
C(20)–C(21)–C(22)	115.2(5)	116.6(6)
C(21)–C(22)–C(23)	131.0(5)	131.6(6)
C(21)–C(22)–N(26)	121.5(5)	120.3(6)
C(23)–C(22)–N(26)	107.5(6)	108.1(6)
C(22)–C(23)–N(24)	108.1(6)	107.0(6)
C(23)–N(24)–C(25)	108.0(7)	108.6(6)
N(24)–C(25)–N(26)	110.6(6)	110.6(6)
C(25)–N(26)–C(22)	105.8(5)	105.6(5)
M–N(26)–C(22)	120.0(4)	119.8(5)
M–N(26)–C(25)	134.1(4)	134.4(4)

TABLE 6

Least-squares planes and atomic deviations (Å) [a]

	M = Zn	M = Cu		M = Zn	M = Cu
Plane 1: N(1)—C(5)					
A	−0.4344	−0.4711	C(2)	−0.005(7)	−0.008(7)
B	0.4500	0.4315	N(3)	0.002(6)	0.005(6)
C	−0.7802	−0.7693	C(4)	−0.002(7)	−0.001(7)
D	14.011	13.527	C(5)	−0.005(6)	−0.004(7)
N(1)	0.006(5)	0.007(5)	M [b]	−0.111(1)	−0.214(1)
Plane 2: C(11)—N(16)					
A	0.2666	0.2838	C(12)	−0.006(7)	−0.009(7)
B	−0.9122	−0.8846	C(13)	0.001(7)	0.005(7)
C	−0.3113	−0.3702	C(14)	0.012(7)	−0.001(7)
D	7.168	8.512	C(15)	−0.019(6)	0.002(7)
C(11)	−0.001(6)	0.010(7)	N(16)	0.014(5)	−0.006(5)
			M [b]	0.112(1)	0.018(1)
Plane 3: C(22)—N(26)					
A	0.5802	0.6020	C(23)	−0.005(8)	−0.011(7)
B	−0.1504	−0.1651	N(24)	0.010(7)	0.005(7)
C	−0.8005	−0.7813	C(25)	−0.011(7)	0.002(7)
D	19.042	18.694	N(26)	0.007(5)	0.009(5)
C(22)	−0.001(6)	0.012(7)	M [b]	−0.076(1)	−0.177(1)
Plane 4: C(7)—C(20)					
A	0.2211	0.2473	C(12)	−0.046(7)	−0.044(7)
B	−0.9271	−0.8955	C(13)	0.027(7)	0.020(7)
C	−0.3027	−0.3700	C(14)	0.083(7)	0.056(7)
D	6.709	8.313	C(15)	0.029(6)	0.048(7)
C(7)	0.150(7)	0.137(7)	N(16)	−0.002(5)	−0.008(5)
N(8)	−0.050(5)	−0.059(5)	C(17)	0.050(6)	0.026(7)
C(9)	−0.054(7)	−0.054(7)	C(18)	−0.013(7)	−0.000(8)
C(10)	−0.043(8)	−0.025(8)	N(19)	0.021(5)	0.008(5)
C(11)	−0.061(6)	−0.033(7)	C(20)	−0.091(6)	−0.072(7)
			M [b]	0.063(1)	0.005(1)
Plane 5: N(8)—N(19), without C(10) and C(18)					
A	0.2464	0.2687	C(12)	−0.029(7)	−0.030(7)
B	−0.9190	−0.8868	C(13)	0.007(7)	0.002(7)
C	−0.3077	−0.3760	C(14)	0.038(7)	0.017(7)
D	6.964	8.572	C(15)	−0.003(6)	0.025(7)
N(8)	0.022(5)	0.009(5)	N(16)	0.002(5)	0.001(5)
C(9)	0.013(7)	0.008(7)	C(17)	−0.003(6)	−0.013(7)
C(11)	−0.033(7)	−0.005(7)	N(19)	−0.015(5)	−0.013(5)
			M [b]	0.085(1)	0.032(1)

Interplanar angles (°)

Planes	M = Zn	M = Cu
1—2	106.5	103.3
1—3	72.3	75.8
1—4	106.1	102.6
1—5	106.3	102.7
2—3	57.2	52.7
2—4	2.8	2.2
2—5	1.2	0.9
3—4	59.3	54.1
3—5	58.2	53.0
4—5	1.6	1.4

[a] The planes are described by the four coefficients of the expression: $Ax + By + Cz + D = 0$. [b] The position of the metal (Zn or Cu) was not included in the calculation of any of the planes.

TABLE 7

Selected torsion angles (°)

	M = Zn	M = Cu
M–N(1)–C(5)–C(6)	−7.41	−11.40
N(1)–C(5)–C(6)–C(7)	66.19	64.66
C(4)–C(5)–C(6)–C(7)	−118.47	−120.91
C(5)–C(6)–C(7)–N(8)	−49.03	−44.82
M–N(8)–C(7)–C(6)	−11.66	−18.96
M–N(19)–C(20)–C(21)	−3.72	0.71
N(19)–C(20)–C(21)–C(22)	−52.71	−54.20
C(20)–C(21)–C(22)–N(26)	62.24	60.11
C(20)–C(21)–C(22)–C(23)	−119.09	−118.85
M–N(26)–C(22)–C(21)	−4.09	−5.58

along the C(13) · · · N(16) vector, except that the angles of orientation of the two imidazole rings with respect to the diacetylpyridine (dap) plane differ by 16° for the zinc structure and 24° in the copper case (see Table 6). Although this ligand has the potential to be highly conjugated from N(8) through N(9) across the pyridyl portion, there is little evidence to support this from the standpoint of observed bond lengths. A similar situation occurred in another dap-containing five-co-ordinate ligand where non-conjugation was attributed to the slight degree of non-planarity which resulted from chelation.[15]

The co-ordination of the Zn and Cu atoms in the present structures would be best described as intermediate between a trigonal bipyramid and a square pyramid, based on the ideal values of the angles.[16] A number of examples are already in the literature.[15,17-20]

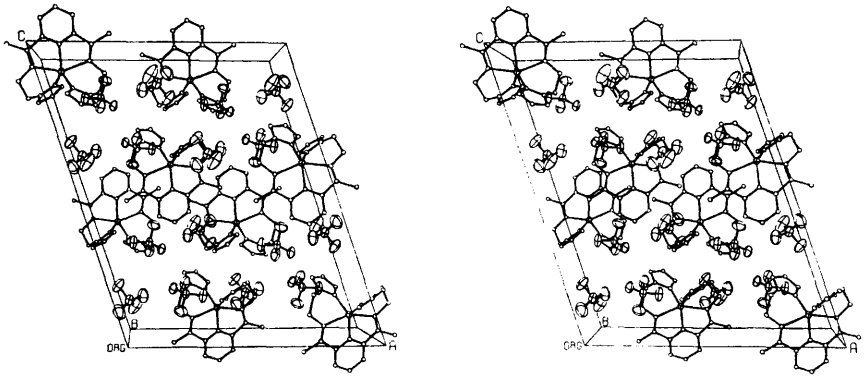

FIGURE 3 Stereoscopic packing diagram of the contents of the unit cell, with hydrogens omitted for clarity. The perchlorate anions are positioned in channels running through the crystal, but they do not seem to be involved in any hydrogen bonding to the imidazole nitrogens

The distortion makes the metal atom a chiral centre, and although the current structures crystallize as a racemic mixture of both possible handednesses, it may eventually be possible to resolve the two optical isomers as has been done with a similar five-co-ordinate zinc complex.[15] The metal–nitrogen distances shown in Table 4 are in the range of those listed for other five-co-ordinate species,[8,15,19-21] but due to the geometric constraints of the ligand itself, some of the distances are as short as those seen in tetrahedral complexes [9,22] or as long as in octahedral complexes.[12,23] In the same environment, one would expect the Cu^{II}–N distances to be slightly shorter than the Zn^{II}–N distances,[8] but this is not observed in the bonds to the imidazoles, which are as long or longer in the copper structure. Since these Cu^{II}–N bonds are still shorter than Cu^{I}–N bonds in five-co-ordinate copper(I) structures,[24] as expected, then this perhaps points to unusually short Zn–imidazole contacts in the current series. The reason for this not obvious, nor is the disparity in Cu–N(imid) lengths noted when the two Zn–N(imid) lengths are the same.

The two independent perchlorate ions in each structure are in excellent agreement with literature results,[25,26] including those in which rotational oscillation corrections were applied.[27-29] The only unusual feature is the short bond Cl(2)–O(5) in each case. This can be explained easily, however, when it is noted in Tables 2 and 3 that O(5) has the largest thermal parameters, and the effect of this apparent oscillation is to shift the centre of density toward the chlorine, resulting in a shorter bond length. The oxygen–N(imid) contacts are all too long to be involved in hydrogen bonding, a conclusion confirmed by the magnitudes of the oxygen thermal parameters which can be seen clearly in Figure 3. There are no unusually short contacts between any other atoms in the molecules.

Finally, on the basis of the present structural study, which establishes $[Zn^{II}(imep)]^{2+}$ and $[Cu^{II}(imep)]^{2+}$ to be well defined five-co-ordinate species, it is possible to speculate more firmly on the structure of the $[Cu^{I}(imep)]^{+}$ oxygen carrier and on the mechanism for its reversible oxygenation. While five-co-ordinate copper(I) species are still relatively rare, a few are now known,[30] and the predisposition of the five nitrogen-donor atoms of the imep ligand suggests that $[Cu^{I}(imep)]^{+}$ will ultimately prove to be five-co-ordinate as well.* Assuming this to be the case, the most reasonable site for initial O_2 ligation appears to be *trans* to the pyridine nitrogen atom and between the two imidazole rings. However, due to steric hindrance with imidazole nitrogens [N(3), N(24)], a bent O_2 ligated at this site would produce a dioxygen adduct (probably more correctly written as Cu^{II}–O_2^-) which could get no stabilization by *intramolecular* [Cu–O_2^- · · · HN(imidazole)] hydrogen-bonding interactions of the type proposed to exist between end-on bonded O_2 in [Fe(haeme)–O_2^-] and the distal histidine imidazole proton in oxymyoglobin and oxyhaemoglobin.[31] On the other hand, the product of dioxygen addition could be a five-co-ordinate species obtained by release of an imidazole ligand from the copper co-ordination sphere at the time of attack by dioxygen. Such a species could then be stabilized by an NH · · · O hydrogen bond between the end-on bonded dioxygen ligand and

* Attempts are presently underway to grow crystals of $[Cu^{I}(imep)]X$ (X = ClO_4 or BF_4) under inert atmospheric conditions.

the hydrogen atom of the ' free ' imidazole. The resulting free space around the metal would also be advantageous for dimer formation of the type discussed below. Finally, an end-on bonded configuration for O_2 is also suggested by the fact that the stoicheiometry of the reversible reaction $2[Cu^{I}(imep)]^{+} + O_2 \rightleftharpoons$ oxy-product implies that the final oxygenated material is binuclear in copper and an end-on bonded μ-dioxygen bridge, *i.e.* Cu^{II}–O–O–Cu^{II}, would probably be necessary to span the distance (5—6 Å) required to bridge the two copper centres. Furthermore, it is possible that the imidazole protons are even more intimately involved in the oxygenation mechanism. For example, the following mechanism, equations (1) and (2), can be written whereby the μ-dioxygen

$$2[Cu^{I}(imep)]^{+} + O_2 \rightleftharpoons [\{Cu^{II}(imep)\}_2(O_2^{2-})]^{2+} \quad (1)$$

$$[\{Cu^{II}(imep)\}_2(O_2^{2-})]^{2+} \rightleftharpoons H_2O_2 + 2[Cu^{II}(imep - H)]^{+} \quad (2)$$

(or μ-peroxo-) species serves as only an intermediate from which proton abstraction can occur to give, for example, H_2O_2 and a mono-deprotonated oxidized copper(II) product, $[Cu^{II}(imep - H)]^{+}$. In fact, a similar deprotonation scheme has recently been proposed for the reaction of O_2 with tris(2,2′-bi-2-imidazoline)iron(II).[32] The final $[Cu^{II}(imep - H)]^{+}$ product would need to be dimerized or polymerized to adequately explain the observed reduction in e.s.r. intensity of the oxy-form,[1-3] and the removal of O_2 would then have to cause spontaneous re-reduction to $[Cu^{I}(imep)]^{+}$ to complete the reversible oxygenation cycle. Additional spectroscopic, product analysis, and structural studies designed to further illucidate mechanistic details of the reversible oxygenation reaction of these unusual copper(I) species are presently being intensely pursued.

Support from the Robert A. Welch Foundation and the U.S. National Science Foundation is gratefully acknowledged. In addition, we thank Professor Joan Valentine for preliminary communication of unpublished work on the $[Cu^{II}(imep)][ClO_4]_2$ compound and for useful comments concerning the possible oxygenation mechanism of $[Cu^{I}(imep)]^{+}$.

[0/1704 *Received*, 7th *November*, 1980]

REFERENCES

[1] M. Simmons and L. J. Wilson, *J. Chem. Soc., Chem. Commun.*, 1978, 634.
[2] L. J. Wilson, C. L. Merrill, M. G. Simmons, J. M. Trantham, L. A. Bottomley, and K. M. Kadish, in ' Invertebrate Oxygen Binding Proteins. Structure, Active Site and Function,' ed. J. Lamy, Marcel Dekker, Inc., New York, 1981.
[3] M. G. Simmons, C. L. Merrill, L. J. Wilson, L. A. Bottomley, and K. M. Kadish, *J. Chem. Soc., Dalton Trans.*, 1980, 1827.
[4] R. G. Wilkins, *Adv. Chem. Ser.*, 1971, **100**, 111; J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235; F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, 1975, **8**, 384; G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1; L. Vaska, *Acc. Chem. Res.*, 1976, **9**, 175; J. A. McGinnety, in ' MTP International Review of Science,' ed. D. W. A. Sharp, University Park Press, Baltimore, 1972, Series One, vol. 5; J. W. Buchler, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 407.
[5] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[7] G. M. Sheldrick, The SHELX System of Crystallographic Programs, Cambridge University, 1976.
[8] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc., Dalton Trans.*, 1972, 1603.
[9] W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1977, **16**, 1119.
[10] B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, 1958, **2**, 361.
[11] G. Sproul and G. D. Stucky, *Inorg. Chem.*, 1973, **12**, 2898.
[12] M. M. Harding and S. J. Cole, *Acta Crystallogr.*, 1963, **16**, 643.
[13] G. Fransson and B. K. S. Lundberg, *Acta Chem. Scand., Ser. A*, 1974, **28**, 578.
[14] M. G. B. Drew and S. Hollis, *Acta Crystallogr., Sect. B*, 1978, **34**, 2853.
[15] V. L. Goedken and G. G. Cristoph, *Inorg. Chem.*, 1973, **12**, 2316.
[16] R. J. Gillespie, *J. Chem. Soc.*, 1963, 4672.
[17] D. Van der Helm, A. F. Nicholas, and C. G. Fisher, *Acta Crystallogr., Sect. B*, 1970, **26**, 1172.
[18] D. Van der Helm and H. B. Nicholas, jun., *Acta Crystallogr., Sect. B*, 1970, **26**, 1858.
[19] A. Mangia, M. Nardelli, C. Palmieri, and G. Pelizzi, *J. Cryst. Mol. Struct.*, 1972, **2**, 99, and refs. therein.
[20] M. Cannas, G. Carta, and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 1974, 550.
[21] A. B. Blake and L. R. Fraser, *J. Chem. Soc., Dalton Trans.*, 1974, 2554.
[22] J. F. Le Querler, M. M. Borel, and A. Leclaire, *Acta Crystallogr., Sect. B*, 1977, **33**, 2299.
[23] C. Sandmark and C.-I. Branden, *Acta Chem. Scand.*, 1967, **21**, 993.
[24] R. R. Gangé, J. L. Allison, R. S. Gall, and C. A. Koval, *J. Am. Chem. Soc.*, 1977, **99**, 7170.
[25] B. Dickens, *Acta Crystallogr., Sect. B*, 1969, **25**, 1875.
[26] M. M. Kadooka, L. G. Warner, and K. Seff, *J. Am. Chem. Soc.*, 1976, **98**, 7569.
[27] M. R. Truter, D. W. J. Cruickshank, and G. A. Jeffrey, *Acta Crystallogr.*, 1960, **13**, 855.
[28] C. E. Nordman, *Acta Crystallogr.*, 1962, **15**, 18.
[29] A. Lopez-Castro and M. R. Truter, *Acta Crystallogr.*, 1964, **17**, 465.
[30] Ref. 24 and refs. therein.
[31] See for example, E. Ochiai, ' Bioinorganic Chemistry,' Allyn and Bacon, Boston, 1977, ch. 6.
[32] M. G. Burnett, V. McKee, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 599.