Preparation and Crystal Structure† of an Imidazolate-bridged Polynuclear Complex $[\{Cu(im)(dien)\}_n][ClO_4]_n$ (dien = diethylenetriamine), and Its Properties in Dimethyl Sulphoxide Solution

Masaaki Sato, Suguru Nagae, Katsumi Ohmae, and Jun-ichi Nakaya *
Department of Chemistry, Faculty of Integrated Arts and Sciences, University of Osaka Prefecture, Mozu Umemachi, Sakai, Osaka 591, Japan
Kunio Miki and Nobutami Kasai *
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

The structure of $[Cu(im)(dien)]ClO_4$ [dien = diethylenetriamine, im = imidazolate], obtained from $[Cu(Him)(dien)][ClO_4]_2$ (Him = imidazole) by deprotonation of the co-ordinated imidazole, was identified by *X*-ray crystallography. The crystals belong to the monoclinic system, space group $P2_1/c$, with $a = 14.341(4)$, $b = 15.473(2)$, $c = 12.822(2)$ Å, $\beta = 114.11(2)°$, and $Z = 8$. The crystal is built up of polynuclear $[Cu(im)(dien)]ClO_4$ units. The geometry around each copper(II) atom is trigonal bipyramidal, comprising the tridentate diethylenetriamine ligand and two imidazolate molecules. The copper(II) atoms are bridged by the imidazolate rings in two alternating orientations, leading to two polynuclear units in each unit cell. In dimethyl sulphoxide solution, $\lambda_{max.}$ for the complex is shifted by more than 30 nm to shorter wavelengths with decreasing concentration. Solution conductivity measurements did not suggest that polymeric ions were present, rather a 1 : 1 electrolyte. A mononuclear copper(II) complex containing imidazolate seems to be formed under dilute conditions by dissociation of the imidazolate bridge.

The imidazole residue of histidine is often found in the active centre of metalloenzymes, and also serves as a ligand for metal ions.[1] Imidazolate, the deprotonated form of imidazole, is involved in the active site of bovine erythrocyte superoxide dismutase.[2] It bridges a copper(II) and a zinc(II) ion. To explore the properties of imidazolate-bridged binuclear complexes, model complexes of the pairs copper–copper,[3–6] copper–cobalt,[7] and copper–zinc[8] have been synthesized and studied extensively. Crystallographic studies of binuclear copper–copper complexes showed that the copper(II) atom has a distorted tetragonal configuration and that the bridging imidazolate lies on the tetragonal plane with its ring plane oriented perpendicular[3,6] or, in some cases, parallel to the tetragonal plane.[9,10] A polynuclear imidazolate-bridged structure is seen in some complexes with additional imidazoles as neutral ligands in the solid state,[11,12] each of the copper(II) atoms being linked by an imidazolate bridge. Although bi- and poly-nuclear imidazolate-bridged copper(II) complexes have been reported, the mononuclear complex with imidazolate is not known either in the solid state or in solution. So it is of interest to synthesize such a complex and to compare its molecular structure with those mentioned above.

In this paper we describe the preparation and crystal structure of the copper(II) complex $[Cu(im)(dien)]ClO_4$, where im = imidazolate and dien = diethylenetriamine, and also its spectrophotometric properties and conductivity in dimethyl sulphoxide solution. This complex is expected to exhibit the characteristic properties of co-ordinated imidazolate acting as a bidentate bridge or as an unidentate ligand. Our main interest here is with the complex structure in the crystal and in solution.

Results and Discussion

Preparation of $[Cu(im)(dien)]ClO_4$.—The complex was obtained by two successive reactions: preparation of a precursor of the copper(II) complex containing imidazole, $[Cu(Him)(dien)][ClO_4]_2$, followed by deprotonation of the pyrrole hydrogen of the co-ordinated imidazole. The deprotonation was done in ethanol solution by the addition of an equimolar amount of a strong base such as sodium ethoxide or 1,8-diazabicyclo[5.4.0]undec-7-ene. The pyrrole hydrogen could also be removed in an alkaline aqueous solution containing a ten-fold excess of sodium hydroxide. The pale blue, fine crystals obtained from ethanol solution and those obtained from the aqueous solution gave the same elemental analysis, but recrystallization to give single crystals suitable for *X*-ray experiments was possible only from the alkaline aqueous solution. By these procedures, we obtained the complex as a single product in good yield. A different method, that of mixing $[Cu(H_2O)(dien)][ClO_4]_2$ with an equimolar amount of sodium imidazolate, did not give the desired complex but rather an imidazolate-bridged binuclear complex, $[Cu_2(im)(dien)_2][ClO_4]_3$, as the main product.

The deprotonation, in aqueous solution seems to be of interest, since it is widely accepted that co-ordination of imidazole to copper(II) is weak and that the imidazole ligand is easily replaced by hydroxide ion in alkaline aqueous solution.[3,4] Our results, on the contrary, show that such replacement does not occur at all even under highly alkaline conditions. Hydroxide ion does not replace the imidazole, but acts as a base to deprotonate the pyrrole hydrogen.

Crystal and Molecular Structure.—The present complex is not mononuclear but polynuclear, of the type in which the Cu atoms are connected to each other through imidazolate bridges to form an infinite chain along the *b* axis. Two polymeric chains run through the unit cell, as shown in the crystal-packing

---

† *Supplementary data available* (No. SUP 56589, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

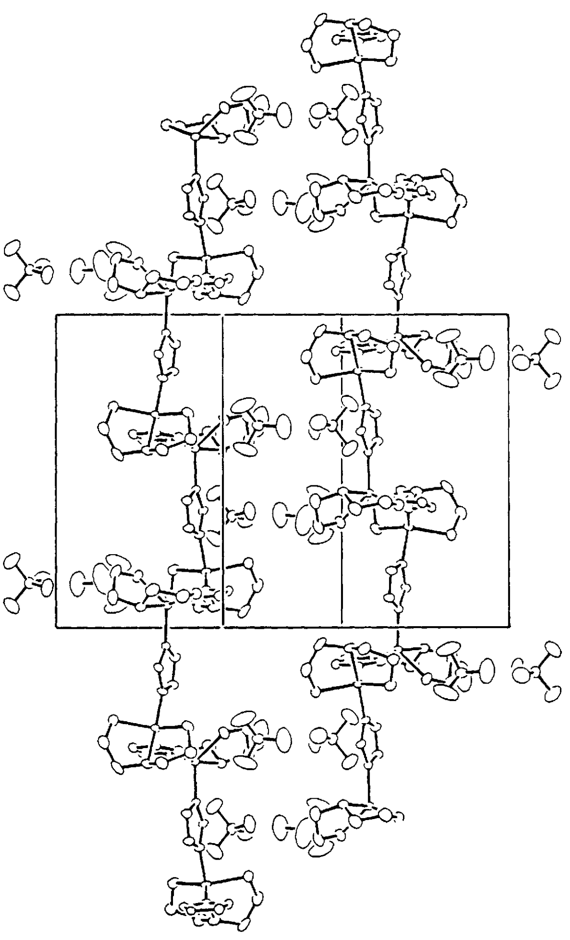


Figure 1. An ORTEP drawing of the crystal structure. Non-hydrogen atoms are represented by thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity

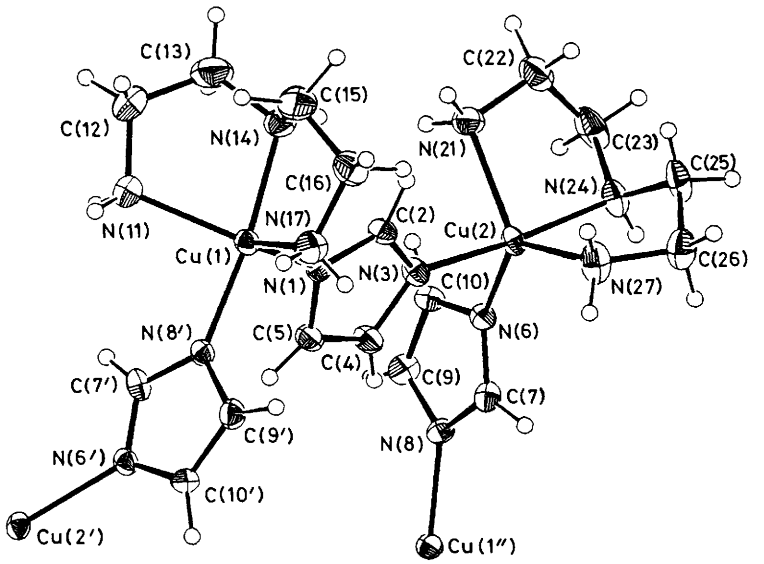


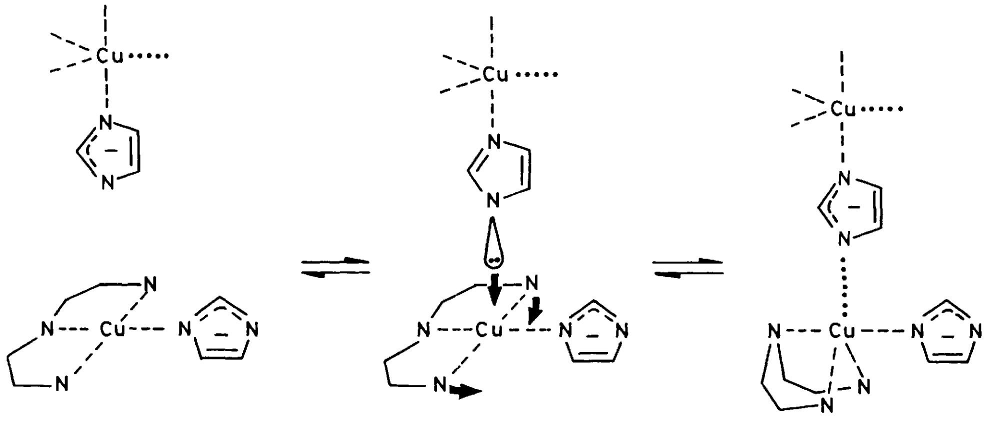
Figure 2. A perspective view of the two types of copper(II) units together with the atom numbering system (ORTEP drawing). Non-hydrogen atoms are represented by thermal ellipsoids at the 30% probability level, hydrogen atoms as spheres of arbitrary radius

diagram in Figure 1. Figure 2 presents the co-ordination geometry of the complex. The geometry around each Cu atom is trigonal bipyramidal, comprising the tridentate ligand diethylenetriamine and two imidazolates. One of the imidazolates is co-ordinated in the trigonal plane and the other at an apical site. There are two types of imidazolate bridges in this polymeric structure. One type is observed in the Cu(1) unit, where an imidazolate nitrogen is co-ordinated to the Cu atom [N(1)–Cu(1)] with the imidazolate-ring plane approximately perpendicular to the trigonal plane (type A imidazolate). The other is seen in the Cu(2) unit, where the imidazolate is co-ordinated to the Cu atom [N(6)–Cu(2)] with the ring plane co-planar to the trigonal plane (type B imidazolate). The dihedral angle between the Cu(1) trigonal plane and the type A imidazolate-ring least-squares plane is 73.1(3)°, while that between Cu(2) and type B planes is 11.6(3)°.

Co-ordination around Cu(1) *and* Cu(2). The atoms located on each of the trigonal planes of the two copper(II) atoms, Cu(1),N(1),N(11),N(17) and Cu(2),N(6),N(21),N(27) are co-planar, with the maximum deviations from the least-squares planes being 0.09(3) and 0.11(3) Å. However, Cu(1) and Cu(2) are respectively 0.12(3) and 0.16(2) Å out of the trigonal planes in the direction of the apical imidazolates. Bond lengths and angles are listed in Table 1. The distances between Cu and the three nitrogen atoms of the diethylenetriamine fall in the range 2.04—2.18 Å. Among these, the copper–secondary nitrogen bonds [Cu(1)–N(14) 2.052(6) and Cu(2)–N(24) 2.041(7) Å] at the apical sites are the shortest in both units. Among the four copper–imidazolate nitrogen bonds, Cu(1)–N(8′) [1.970(5) Å] and Cu(2)–N(3) [1.984(6) Å] at the apical sites are shorter than Cu(1)–N(1) [2.057(5) Å] and Cu(2)–N(6) [2.064(6) Å] on the trigonal plane. For type A and type B imidazolates, there is no significant difference in the co-ordination bond distances. These copper–imidazolate bond distances are longer than those of similar bi- and poly-nuclear complexes, *e.g.* 1.944(12) and 1.966(14) Å in $[Cu_2(im)(ClO_4)_2(Me_2NCH_2CH_2NHCH_2CH_2NMe_2)_2]ClO_4$,[3] 1.928(3) and 1.940(3) Å in $Na[Cu_2(Gly\text{-}GlyO)_2(im)]$,[9] and 1.963(5) and 1.986(5) Å in $[Cu(Him)_2(im)(Cl)]$.[12] This suggests that the imidazolate nitrogen atom may have weaker co-ordination to the Cu atom at the trigonal plane sites. The polynuclear structure may be constructed from a single unit of $[Cu(im)(dien)]ClO_4$ by intermolecular approach of the imidazolate to another Cu atom, two Cu–N

Table 1. Bond distances (Å) and angles (°) of [Cu(im)(dien)]ClO$_4$ along with their estimated standard deviations in parentheses

Cu(1)–N(1)	2.057(5)	Cu(1)–N(8′)	1.970(5)	N(11)–C(12)	1.459(12)	C(12)–C(13)	1.520(14)
Cu(1)–N(11)	2.105(7)	Cu(1)–N(14)	2.052(6)	C(13)–N(14)	1.496(12)	N(14)–C(15)	1.486(11)
Cu(1)–N(17)	2.147(7)	Cu(2)–N(3)	1.984(6)	C(15)–C(16)	1.498(12)	C(16)–N(17)	1.474(11)
Cu(2)–N(6)	2.064(6)	Cu(2)–N(21)	2.174(6)	N(21)–C(22)	1.471(10)	C(22)–C(23)	1.490(12)
Cu(2)–N(24)	2.041(7)	Cu(2)–N(27)	2.054(8)	C(23)–N(24)	1.475(11)	N(24)–C(25)	1.493(11)
N(1)–C(2)	1.333(8)	N(1)–C(5)	1.376(8)	C(25)–C(26)	1.504(13)	C(26)–N(27)	1.482(12)
C(2)–N(3)	1.346(8)	N(3)–C(4)	1.365(9)	Cl(1)–O(11)	1.417(9)	Cl(1)–O(12)	1.415(9)
C(4)–C(5)	1.359(9)	N(6)–C(7)	1.327(9)	Cl(1)–O(13)	1.374(8)	Cl(1)–O(14)	1.414(8)
N(6)–C(10)	1.363(8)	C(7)–N(8)	1.342(9)	Cl(2)–O(21)	1.374(12)	Cl(2)–O(22)	1.363(13)
N(8)–C(9)	1.360(9)	C(9)–C(10)	1.367(10)	Cl(2)–O(23)	1.374(14)	Cl(2)–O(24)	1.334(15)
N(1)–Cu(1)–N(8′)	92.9(2)	N(1)–Cu(1)–N(11)	126.6(3)	N(8)–C(9)–C(10)	108.6(6)	N(6)–C(10)–C(9)	108.6(6)
N(1)–Cu(1)–N(14)	96.2(3)	N(1)–Cu(1)–N(17)	114.6(3)	Cu(1)–N(11)–C(12)	112.1(5)	N(11)–C(12)–C(13)	109.5(8)
N(8′)–Cu(1)–N(11)	91.9(3)	N(8′)–Cu(1)–N(14)	170.8(3)	C(12)–C(13)–N(14)	108.9(8)	Cu(1)–N(14)–C(13)	108.7(5)
N(8′)–Cu(1)–N(17)	95.2(3)	N(11)–Cu(1)–N(14)	81.7(3)	Cu(1)–N(14)–C(15)	108.3(5)	C(13)–N(14)–C(15)	112.5(7)
N(11)–Cu(1)–N(17)	117.8(3)	N(14)–Cu(1)–N(17)	82.0(3)	N(14)–C(15)–C(16)	108.8(7)	C(15)–C(16)–N(17)	108.9(7)
N(3)–Cu(2)–N(6)	93.6(3)	N(3)–Cu(2)–N(21)	94.7(3)	Cu(1)–N(17)–C(16)	108.7(5)	Cu(2)–N(21)–C(22)	108.6(5)
N(3)–Cu(2)–N(24)	173.5(3)	N(3)–Cu(2)–N(27)	94.4(3)	N(21)–C(22)–C(23)	108.9(7)	C(22)–C(23)–N(24)	110.3(7)
N(6)–Cu(2)–N(21)	107.9(3)	N(6)–Cu(2)–N(24)	92.5(3)	Cu(2)–N(24)–C(23)	109.6(5)	Cu(2)–N(24)–C(25)	107.3(5)
N(6)–Cu(2)–N(27)	127.5(3)	N(21)–Cu(2)–N(24)	81.5(3)	C(23)–N(24)–C(25)	114.1(7)	N(24)–C(25)–C(26)	108.8(7)
N(21)–Cu(2)–N(27)	122.9(3)	N(24)–Cu(2)–N(27)	83.4(3)	C(25)–C(26)–N(27)	107.1(7)	Cu(2)–N(27)–C(26)	110.4(6)
Cu(1)–N(1)–C(2)	132.3(5)	Cu(1)–N(1)–C(5)	123.8(4)	O(11)–Cl(1)–O(12)	105.5(5)	O(11)–Cl(1)–O(13)	109.4(5)
C(2)–N(1)–C(5)	103.8(5)	N(1)–C(2)–N(3)	113.8(6)	O(11)–Cl(1)–O(14)	106.4(5)	O(12)–Cl(1)–O(13)	112.1(5)
Cu(2)–N(3)–C(2)	127.7(5)	Cu(2)–N(3)–C(4)	127.6(5)	O(12)–Cl(1)–O(14)	110.0(5)	O(13)–Cl(1)–O(14)	113.0(5)
C(2)–N(3)–C(4)	104.7(6)	N(3)–C(4)–C(5)	108.2(6)	O(21)–Cl(2)–O(22)	109.8(8)	O(21)–Cl(2)–O(23)	105.4(8)
N(1)–C(5)–C(4)	109.5(6)	Cu(2)–N(6)–C(7)	126.7(5)	O(21)–Cl(2)–O(24)	112.3(8)	O(22)–Cl(2)–O(23)	105.9(8)
Cu(2)–N(6)–C(10)	125.2(5)	C(7)–N(6)–C(10)	104.8(6)	O(22)–Cl(2)–O(24)	111.6(9)	O(23)–Cl(2)–O(24)	111.4(9)
N(6)–C(7)–N(8)	113.6(6)	C(7)–N(8)–C(9)	104.5(6)				



Scheme.

bonds with the diethylenetriamine bending toward the opposite side of the incoming imidazolate to form a new trigonal plane. A possible mechanism for this intermolecular complexation is illustrated in the Scheme.

Properties in Dimethyl Sulphoxide Solution.—The complex was soluble in dimethyl sulphoxide. Metal complexes which exhibit neither intermolecular metal–metal interaction nor structural alteration upon concentration in solution usually follow Beer's law and $\lambda_{max.}$ in their absorption spectra would not change upon dilution of their solutions. This is the case for the imidazolate-bridged binuclear copper(II) complex [Cu$_2$(im)(dien)$_2$][ClO$_4$]$_3$, for which $\lambda_{max.}$ is constant at 588 nm (Figure 3) and the absorbance increases linearly with copper(II) concentration from 0.1×10^{-2} to 1.5×10^{-2} mol dm^{-3}. In the case of the polynuclear complex, however, $\lambda_{max.}$ shifted by more than 30 nm to longer wavelengths with increasing concentration (Figure 3) and the absorbance at 586 and at 622 nm did not obey Beer's law. This suggests a marked structural change when the complex is dissolved in dimethyl sulphoxide.

The solution conductivity was measured to identify the electrolyte type and the structure of the complex in dimethyl sulphoxide solution. The equivalent conductivity (Λ_e) was plotted as a function of $\sqrt{c}$, and both the equivalent conductivity at infinite dilution (Λ_0) and the slope (A) of the Onsager plot are given in Table 2. The copper(II) complex [Cu(Him)(dien)][ClO$_4$]$_2$ behaves as a 1:2 electrolyte and [Cu$_2$(im)(dien)$_2$][ClO$_4$]$_3$ as a 1:3 electrolyte. When polymeric ions are present in the solution, they can easily be recognized by the large slope A.[13] The present complex has a smaller slope A than would be expected from its polynuclear structure. This value does not suggest that there are any polymeric ions, but

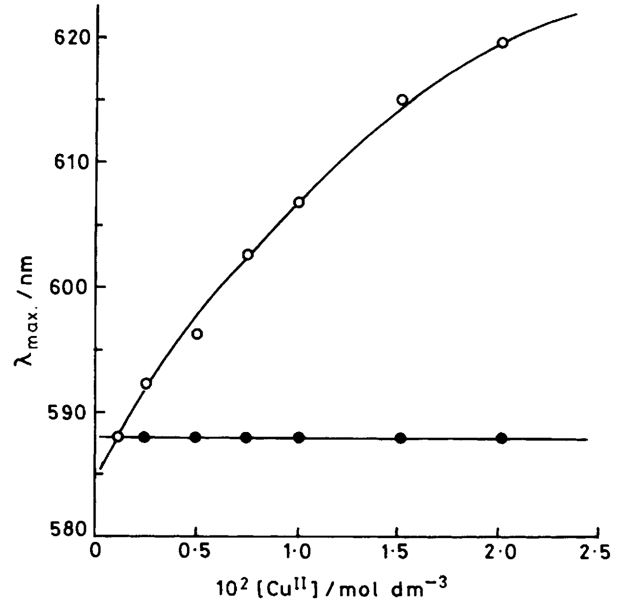


Figure 3. Dependence of $\lambda_{max.}$ on the copper(II) concentration of [Cu(im)(dien)]ClO$_4$ (○) and [Cu$_2$(im)(dien)$_2$][ClO$_4$]$_3$ (●) in dimethyl sulphoxide

rather that there is a 1:1 electrolyte in solution, produced by breaking the intermolecular imidazolate bridges of the polynuclear complex. Since the degree of dissociation seems to depend on the concentration of the complex in the solution, judging from the absorption spectra, the conductivities observed may be derived from various complex species, among which the mononuclear complex is the most common in dilute conditions. The possibility of dissociation induced by traces of water was excluded, since the solvent was highly purified and the water content seemed to be less than 1% of that of the complex. When water was added to a solution of the complex the imidazolate became protonated to give [Cu(Him)(dien)]$^{2+}$, which was not observed at all in the above solutions. Both the small slope A and the small Λ_e at various concentrations indicate that there is molecular dissociation of the polynuclear structure by breakage of the intermolecular imidazolate bridges, resulting in the formation of the mononuclear imidazolato-copper complex in solution. These results indicate that this new type of complex may also be present in some metalloenzymes where the imidazole residue of histidine is co-ordinated to the metal ion.

Experimental

All reagents were of the highest grade commercially available. Dimethyl sulphoxide was purified by repeated fractional distillation from granular calcium hydride under reduced pressure and stored over molecular sieves. It had a conductance of the order of 10^{-8} S cm^{-1}. Electronic spectra were recorded at 25 °C in dimethyl sulphoxide solution on a Hitachi 228 spectrophotometer equipped with a water-circulating thermostat system. Conductivities were measured at ambient temperature in dimethyl sulphoxide solution with a TOA CM-1DB conductimeter. Using the Onsager limiting law, $\Lambda_0 - \Lambda_e = A\sqrt{c}$, the value of Λ_0 was determined by extrapolation of a plot of Λ_e against $\sqrt{c}$, where c is the concentration of the complex. The value of A was found from the slope of this linear relationship.

Table 2. Equivalent conductivity data for the complexes in dimethyl sulphoxide

Complex	Λ_0 [a]	A [b]
[Cu(im)(dien)]ClO$_4$	68	73
[Cu(Him)(dien)][ClO$_4$]$_2$	80	204
[Cu$_2$(im)(dien)$_2$][ClO$_4$]$_3$	117	342

[a] Values in S cm^2 mol^{-1} extrapolated to infinite dilution. [b] Slope of the Onsager plot.

Preparation of the Precursor Complex.—To a solution of Cu(ClO$_4$)$_2$·6H$_2$O (0.742 g, 2.0 mmol) in methanol–acetonitrile (5:1, 30 cm^3) were added diethylenetriamine (0. 206 g, 2.0 mmol) in water (3 cm^3) and then imidazole (0.136 g, 2.0 mmol) in methanol (10 cm^3). After being left overnight, dark blue *crystals* of [Cu(Him)(dien)][ClO$_4$]$_2$ were collected by filtration, washed with ethanol, and dried *in vacuo*. Yield 0.650 g (75%) (Found: C, 19.55; H, 4.05; Cl, 16.5; Cu, 14.8; N, 16.15. $C_7H_{17}Cl_2CuN_5O_8$ requires C, 19.4; H, 3.95; Cl, 16.35; Cu, 14.65; N, 16.15%).

Preparation of the Copper(II) *Complex containing Imidazolate.*—(*a*) *From ethanol solution.* To a well stirred solution of the precursor complex [Cu(Him)(dien)][ClO$_4$]$_2$ (0.434 g, 1.0 mmol) in ethanol (30 cm^3) was added dropwise sodium ethoxide (1.0 cm^3 of a 1.0 mol dm^{-3} solution in ethanol, 1.0 mmol). The solution was stirred for 1 h, when pale blue micro-*crystals* of [Cu(im)(dien)]ClO$_4$ were filtered off, washed with ethanol, and dried *in vacuo*. Yield 0.266 g (80%) (Found: C, 25.1; H, 4.8; Cl, 10.4; N, 20.85. $C_7H_{16}ClCuN_5O_4$ requires C, 25.1; H, 4.8; Cl, 10.65; N, 21.0%).

(*b*) *From aqueous solution.* To a well stirred solution of [Cu(Him)(dien)][ClO$_4$]$_2$ (0.434 g, 1.0 mmol) in water (20 cm^3) was added sodium hydroxide (4.000 g, 10.0 mmol) in water (20 cm^3). The mixture was stored overnight to give blue crystals of [Cu(im)(dien)]ClO$_4$. Yield 0.213 g (64%) (Found: C, 25.35; H, 4.95; Cl, 10.5; N, 21.1%). Recrystallization of the complex from water afforded a dark blue crystal suitable for *X*-ray diffraction study.

Crystallography.—*Crystal data.* $C_7H_{16}ClCuN_5O_4$, M = 333.24, monoclinic, a = 14.341(4), b = 15.473(2), c = 12.822(2) Å, β = 114.11(2)°, U = 2 596.9(9) Å^3 (by least-squares fit of the 2θ values of 25 reflections accurately measured on a diffractometer, λ = 0.710 69 Å), space group $P2_1/c$, Z = 8, D_c = 1.705 g cm^{-3}, approximate dimensions 0.38 × 0.25 × 0.13 mm, μ(Mo-K_α) = 19.7 cm^{-1}, F(000) = 1 368.

Structure determination. Intensity data were collected on a Rigaku automated, four-circle diffractometer by the θ—2θ scan technique using graphite-monochromatized Mo-K_α radiation. The scan width and speed were $\Delta 2\theta = (1.8 + 1.70 \tan\theta)°$ and 4° min^{-1}, respectively. Background intensities were measured for 7.5 s at both ends of a scan. A total of 5 664 reflections was measured with 2θ up to 54°, 3 995 of which had $|F_o| > 3\sigma(|F_o|)$. The usual Lorentz and polarization corrections were made, but no correction for absorption was made, because of the low absorbance.

The structure was solved by the heavy-atom method. The refinement was carried out by block-diagonal least squares using HBLS-V program,[14] the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on a Fourier difference map, the parameters of which were further refined isotropically, but the isotropic thermal parameters were fixed at the values of the equivalent isotropic thermal parameters[15] of the bonded C and N atoms. 424 Parameters were refined at the

Table 3. Fractional atomic co-ordinates along with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.161 96(6)	0.571 60(5)	0.442 27(6)	N(17)	0.150 4(5)	0.609 2(4)	0.597 7(5)
Cu(2)	0.214 06(6)	0.179 34(5)	0.466 62(6)	N(21)	0.363 5(4)	0.204 8(4)	0.467 6(5)
N(1)	0.144 7(4)	0.441 3(3)	0.408 0(4)	C(22)	0.433 2(6)	0.134 7(6)	0.530 1(7)
C(2)	0.201 2(5)	0.373 1(4)	0.460 4(5)	C(23)	0.374 1(7)	0.052 7(6)	0.511 0(7)
N(3)	0.160 0(4)	0.296 8(3)	0.413 6(4)	N(24)	0.283 1(5)	0.065 2(4)	0.535 6(5)
C(4)	0.071 1(5)	0.318 0(4)	0.323 7(5)	C(25)	0.305 5(7)	0.067 4(5)	0.660 0(6)
C(5)	0.061 6(5)	0.405 5(4)	0.320 5(5)	C(26)	0.213 5(7)	0.102 0(5)	0.674 3(7)
N(6)	0.124 8(4)	0.122 0(3)	0.312 6(4)	N(27)	0.186 0(5)	0.185 0(4)	0.611 2(5)
C(7)	0.024 6(5)	0.109 0(4)	0.270 7(5)	Cl(1)	0.537 37(12)	0.643 86(11)	0.263 34(14)
N(8)	−0.018 1(4)	0.096 6(3)	0.157 2(4)	O(11)	0.583 5(6)	0.571 0(5)	0.236 7(7)
C(9)	0.061 2(5)	0.101 5(4)	0.125 3(6)	O(12)	0.601 5(6)	0.714 7(5)	0.268 2(6)
C(10)	0.148 7(5)	0.117 2(4)	0.220 3(5)	O(13)	0.440 4(5)	0.654 4(5)	0.180 2(7)
N(11)	0.214 3(5)	0.664 4(4)	0.358 7(5)	O(14)	0.538 8(5)	0.628 2(5)	0.372 7(6)
C(12)	0.324 4(6)	0.677 8(6)	0.416 4(8)	Cl(2)	0.129 60(15)	0.645 37(11)	0.008 38(15)
C(13)	0.374 6(6)	0.597 0(7)	0.483 3(8)	O(21)	0.055 7(8)	0.708 5(6)	−0.027 4(9)
N(14)	0.314 5(4)	0.566 8(4)	0.548 2(5)	O(22)	0.176 5(8)	0.640 5(8)	−0.064 8(8)
C(15)	0.332 2(6)	0.621 1(6)	0.650 1(7)	O(23)	0.077 6(10)	0.568 9(6)	−0.003 7(11)
C(16)	0.251 9(6)	0.600 6(6)	0.692 9(6)	O(24)	0.196 8(7)	0.657 3(10)	0.116 0(7)

final stage. The weighting scheme used in the final refinement was $w = (\sigma_{cs} - 0.0010|F_o| + 0.0018|F_o|^2)^{\frac{1}{2}}$, where σ_{cs} is the standard deviation estimated from the counting statistics. However, at the early stage of the refinement, unit weights were employed. Atomic scattering factors used were taken from ref. 16. The final *R* and *R′* values were 0.061 and 0.071, respectively. Final atomic co-ordinates are given in Table 3.

All the computations were done on an ACOS 850 computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University.

References

1 G. L. Eichhorn and L. G. Marzilli (eds.), 'Advances in Inorganic Biochemistry,' Elsevier/North-Holland, New York, 1979, vol. 1; G. L. Eichhorn (ed.), 'Inorganic Biochemistry,' Elsevier, Amsterdam, 1973, vol. 1.

2 J. M. McCord and I. Fridovich, *J. Biol. Chem.*, 1969, **244**, 6049; H. M. Steinman, in 'Superoxide Dismutase,' ed. L. W. Oberley, CRC Press, Boca Raton, 1982, vol. 1, p. 11.

3 C-L. O'Young, J. C. Dewan, H. R. Lilienthal, and S. J. Lippard, *J. Am. Chem. Soc.*, 1978, **100**, 7291.

4 G. Kolks, C. R. Frihart, P. K. Coughlin, and S. J. Lippard, *Inorg. Chem.*, 1981, **20**, 2933.

5 P. K. Coughlin and S. J. Lippard, *Inorg. Chem.*, 1984, **23**, 1446; P. K. Coughlin, S. J. Lippard, A. E. Martin, and J. E. Bulkowski, *J. Am. Chem. Soc.*, 1980, **102**, 7616.

6 G. Kolks, C. R. Frihart, H. N. Rabinowitz, and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 5720; P. K. Coughlin, J. C. Dewan, S. J. Lippard, E. Watanabe, and J-M. Lehn, *ibid.*, 1979, **101**, 265.

7 W. M. Davis, J. C. Dewan, and S. J. Lippard, *Inorg. Chem.*, 1981, **20**, 2928.

8 M. Sato, S. Nagae, M. Uehara, and J. Nakaya, *J. Chem. Soc., Chem. Commun.*, 1984, 1661.

9 Y. Nakao, W. Mori, T. Sakurai, and A. Nakahara, *Inorg. Chim. Acta*, 1981, **55**, 103; K. Matsumoto, S. Ooi, Y. Nakao, W. Mori, and A. Nakahara, *J. Chem. Soc., Dalton Trans.*, 1981, 2045.

10 J. C. Dewan and S. J. Lippard, *Inorg. Chem.*, 1980, **19**, 2079.

11 G. Ivarsson, B. K. S. Lundberg, and N. Ingri, *Acta Chem. Scand.*, 1972, **26**, 3005.

12 B. K. S. Lundberg, *Acta Chem. Scand.*, 1972, **26**, 3902.

13 R. K. Boggess and D. A. Zatko, *J. Chem. Educ.*, 1975, **52**, 649.

14 T. Ashida, HBLS-V, 'The Universal Crystallographic Computing System-Osaka,' The Computation Centre, Osaka University, 1979, p. 53.

15 W. C. Hamilton, *Acta Crystallogr.*, 1959, **12**, 609.

16 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 71.

Received 28*th October* 1985; *Paper* 5/1876