Crystal and Molecular Structure of Sodium μ-(Imidazol-1-yl-*NN'*)-bis[(glycylglycinato-*NN'O*)cuprate(II)] Hexahydrate: Structure–Magnetism Relationship in Imidazolate-bridged Binuclear Copper(II) Complexes

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The structure of the title complex, $Na[Cu_2(Gly\text{-}GlyO)_2(im)]\cdot 6H_2O$ [Gly-GlyO = glycylglycinate(2−), im = imidazolyl), has been determined from *X*-ray diffractometer data, to give final discrepancy indices of $R = 0.0302$, and $R' = 0.0391$. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions $a = 11.246(4)$, $b = 10.464(3)$, $c = 10.858(4)$ Å, $\alpha = 109.99(3)$, $\beta = 115.05(3)$, $\gamma = 85.05(3)°$, and $Z = 2$. Each copper(II) atom has square-planar co-ordination by amino-nitrogen, deprotonated amide nitrogen, carboxylate oxygen of the glycylglycinate ligand, and by nitrogen of bridging imidazolate, to form altogether a binuclear copper(II) complex. The complex is almost planar and has an approximate two-fold axis which is coincident with that of the imidazolate ring. Variable-temperature magnetic susceptibility data measured down to 4.2 K show an antiferromagnetic exchange interaction with a coupling constant $J = -19$ cm^{-1}. The bridging imidazolate plane and copper(II) co-ordination planes make an angle of 5.8° for Cu(1) and 10.4° for Cu(2). The relative orientation of the bridging imidazolate and the copper(II) co-ordination planes does not seem to be responsible for the magnitude of the magnetic exchange coupling constant ($J = -19$ cm^{-1}) in this case. It is concluded that a π-exchange mechanism is not important in the imidazolate-bridged binuclear copper(II) complexes.

IMIDAZOLATE-bridged bi- and tetra-nuclear copper(II) complexes are of interest as models for the active site of bovine erythrocyte superoxide dismutase. The complex $Na[Cu_2(Gly\text{-}GlyO)_2(im)]\cdot 6H_2O$ was first prepared by Driver and Walker.[1] On the basis of the spectroscopic data, they concluded that one each of imidazolate and hydroxide ions bridge the two copper(II) ions, and the glycylglycinate is co-ordinated to each copper(II) through terminal amino-nitrogen and amide oxygen, whereas the terminal carboxylate oxygen is not co-ordinated.

Recently three of us (Y. N., W. M., and A. N.) reinvestigated the same complex [2] and proposed that the two copper(II) ions are bridged by imidazolate, but not by a hydroxyl group, and glycylglycinate is co-ordinated to each copper(II) through terminal amino-nitrogen, deprotonated amide nitrogen, and terminal carboxylate oxygen. We also demonstrated that there is an antiferromagnetic spin–spin interaction ($J = -19$ cm^{-1}, where J denotes the exchange integral which is defined by the following Hamiltonian, $\mathscr{H} = -2JS_1\cdot S_2$) between the two copper(II) ions in the complex.

Since we are interested in the structure of the complex in connection with the antiferromagnetic interaction, the *X*-ray structure analysis of the complex was undertaken.

EXPERIMENTAL

X-Ray Data Collection.—The crystals were prepared by the method described by Driver and Walker.[1] Preliminary *X*-ray photographic data indicated that the space group was $P\bar{1}$ or $P1$. The space group $P\bar{1}$ was assumed throughout the structure analysis and confirmed by the successful refinement of the structure. The unit-cell dimensions were obtained by the least-squares analysis of 66 θ values automatically centred on a Philips PW1100 four-circle diffractometer.

Crystal Data.—$Na[Cu_2(C_4H_6O_3N_2)_2(C_3H_3N_2)]\cdot 6H_2O$, $M = 585.5$, Triclinic, $a = 11.246(4)$, $b = 10.464(3)$, $c = 10.858(4)$ Å, $\alpha = 109.99(3)$, $\beta = 115.05(3)$, $\gamma = 85.05(3)°$, $U = 1\,085.1(6)$ Å^3, $F(000) = 600$, $D_m = 1.76$ g cm^{-3} (flotation), $Z = 2$, $D_c = 1.79$ g cm^{-3}, space group $P\bar{1}$, $\mu(\text{Mo-}K_\alpha) = 21.3$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å.

The size of specimen employed for data collection was 0.15 × 0.20 × 0.45 mm. The intensity data ($2\theta \leqslant 50°$) were collected at room temperature by the use of graphite-monochromated Mo-K_α radiation. The ω—2θ scan mode was employed. The scan range was $(1.0 + 0.2\tan\theta)°$, and the scan speed, 0.025° s^{-1}; the background was counted for 20 s at each side of the scan range. During the data collection, the intensities of three standard reflections were monitored every 180 min in order to check the orientation and stability of the crystal. No appreciable decay was observed. A total of 3 000 reflections having $F_o^2 \geqslant 3\sigma(F_o^2)$ were considered as observed. The intensities were corrected for Lorentz-polarization effects [3] but not for absorption.

Structure Solution and Refinement.—The two copper atoms were located from a Patterson synthesis. The other non-hydrogen atom positions were obtained from succesive difference-Fourier syntheses. The electron density of one water molecule of crystallization indicated disorder. It was possible, however, to resolve the water molecule into two with an occupancy of 0.5 [O(12) and O(13)]. The block-diagonal least-squares refinement with anisotropic temperature factors for all the non-hydrogen atoms gave $R = 0.0421$ and $R' = [\Sigma w\Delta F^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.0651$. Hydrogen atoms defined by the geometry of the complex were located at calculated positions (N–H, C–H 1.0 Å), while those of water molecules (except the disordered one) were found on a difference-Fourier map. Continued refinement converged at $R = 0.0302$ and $R' = 0.0391$. In the final cycles of the refinement, the hydrogen atoms were included with a common isotropic temperature factor $U = 0.05$ Å^2, but their parameters were not refined. The function minimized was $\Sigma w(F_o - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ was used. All the parameter shifts were less than 0.5σ. The

TABLE 1

Atomic co-ordinates ($\times 10^5$ for Cu and $\times 10^4$ for others) of non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu(1)	−15 014(4)	39 748(4)	−17 983(5)
Cu(2)	12 669(4)	11 793(4)	22 993(4)
N(1)	−1 686(3)	4 777(3)	−3 183(3)
N(2)	−3 198(3)	4 851(3)	−1 897(3)
N(3)	2 584(3)	90(3)	3 135(3)
N(4)	591(3)	1 055(3)	3 725(2)
N(5)	−1 194(3)	3 217(3)	−309(3)
N(6)	−157(2)	2 098(3)	1 227(3)
C(1)	343(3)	3 698(3)	−2 940(4)
C(2)	−672(3)	4 552(4)	−3 702(4)
C(3)	−2 556(3)	5 675(3)	−3 431(4)
C(4)	−3 480(3)	5 799(4)	−2 725(4)
C(5)	3 266(3)	291(3)	1 383(4)
C(6)	3 594(3)	−260(3)	2 606(4)
C(7)	2 444(3)	−466(3)	3 962(4)
C(8)	1 298(3)	13(4)	4 361(4)
C(9)	−125(3)	2 589(3)	261(4)
C(10)	−1 970(3)	3 116(4)	351(4)
C(11)	−1 350(3)	2 432(4)	1 276(4)
O(1)	143(2)	3 329(2)	−2 038(3)
O(2)	1 300(3)	3 384(3)	−3 248(3)
O(3)	−2 669(3)	6 417(3)	−4 167(3)
O(4)	2 220(2)	938(2)	1 051(2)
O(5)	4 007(2)	105(3)	763(3)
O(6)	3 130(3)	−1 352(3)	4 441(3)
O(7)	7 091(3)	1 756(3)	3 280(3)
O(8)	6 886(3)	4 526(3)	3 042(3)
O(9)	5 193(2)	7 342(3)	4 004(4)
O(10)	6 295(4)	7 889(4)	2 391(5)
O(11)	8 293(2)	8 978(3)	1 658(3)
O(12) *	4 754(8)	3 162(10)	428(9)
O(13) *	4 880(7)	4 530(7)	280(8)
Na	6 194(1)	9 626(2)	1 429(2)

* Site occupation factor 0.5.

atomic scattering factors for Cu, Na$^+$, O, N, C, and H were taken from ref. 4, with correction for anomalous scattering for the Cu atom. The final difference-Fourier map was featureless and showed no peaks greater than 0.4 e Å^{-3}, which was located near O(12). The final atomic co-ordinates are given in Table 1. Observed and calculated structure factors, thermal parameters, and hydrogen atom co-ordinates are in Supplementary Publication No. SUP 23098 (10 pp.).*

The computer programs used in the calculations included the local version of UNICS.[5] Figures 1 and 2 were drawn by the use of ORTEP. Calculations were performed on a FACOM 230-60 computer at Osaka City University and on an ACOS-700 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

RESULTS AND DISCUSSION

Crystal Structure.—Two views of the binuclear copper(II) complex are shown in Figure 1(*a*) and (*b*). The complex is almost planar [Figure 1(*b*)] and has an approximate two-fold axis which is coincident with that of the imidazolate ring; two carboxylate groups of the glycylglycinate ligands are disposed in *cis* positions [Figure 1(*a*)]. Each copper(II) atom displays a square-planar co-ordination by terminal amino-nitrogen, deprotonated amide nitrogen, terminal carboxylate oxygen of the glycylglycinate ligand, and nitrogen of the bridging imidazolate, by which a binuclear copper(II) complex is formed. One axial site of each copper(II) is occupied by an amide oxygen of an adjacent complex. The Cu(1)–O(6) and Cu(2)–O(3) distances are 3.186(3) and 2.723(3) Å respectively (Figure 2). The latter value is within the range of semi-co-ordination which describes the axial Cu–O bond in the tetragonally distorted octahedral geometry of Cu^{II}.[6] The intramolecular Cu(1) · · · Cu(2) distance is 5.800(1) Å. The imidazolate ring is planar within ± 0.003 Å (Table 2); Cu(1) is 0.08 Å out of this plane, while Cu(2) deviates 0.06 Å from the plane on the opposite side. The angles between the imidazolate ring and the copper(II) co-ordination planes are 5.8° for Cu(1) and 10.4° for Cu(2). The two copper(II) co-ordination planes make an angle of 5.9°. The bond distances for Cu–N(amino), Cu–N(amide), and Cu–O(carboxylate) are in agreement with those previously reported.[7,8] The Cu–N(imidazolate) distance is slightly shorter than those in

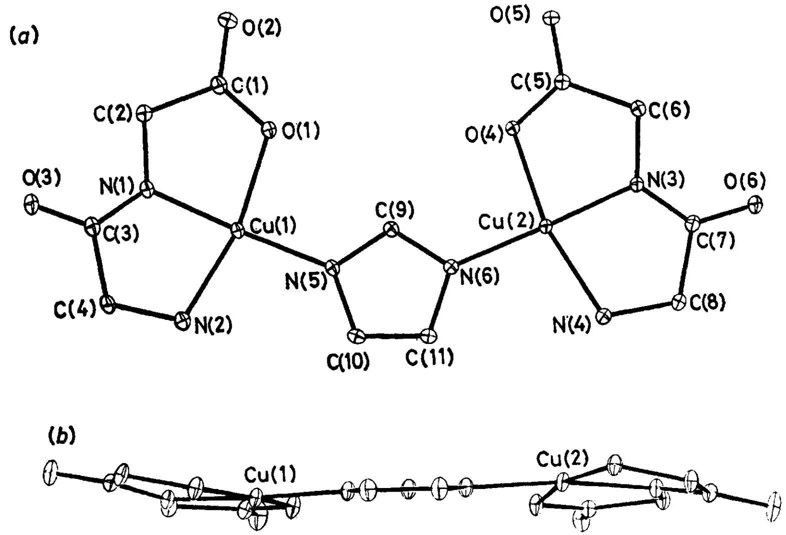

FIGURE 1 Two views (*a*) and (*b*) of the complex anion, [Cu$_2$(Gly-GlyO)$_2$(im)]$^-$, showing the atomic numbering. The thermal ellipsoid was drawn at the 50% probability level

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

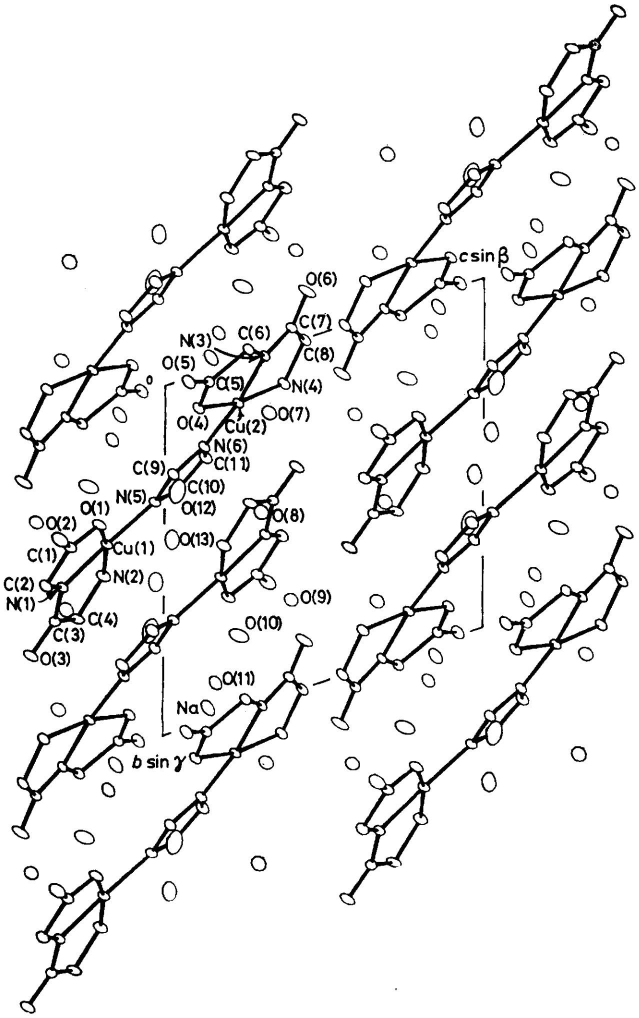

FIGURE 2 Crystal structure of Na[Cu$_2$(Gly-GlyO)$_2$(im)]·6H$_2$O viewed along the *a* axis

TABLE 2

Least-squares planes. *X*, *Y*, and *Z* are orthogonal co-ordinates (Å) relative to *a*, $c^* \times a$, and *c** axes respectively; deviations (Å) of the atoms from the planes are given in square brackets

Plane (1): N(5), N(6), C(9), C(10), C(11)

$$-0.1925X - 0.6568Y - 0.7291Z + 1.8875 = 0$$

[N(5) 0.001, N(6) −0.003, C(9) 0.001, C(10) −0.003, C(11) 0.003, Cu(1) 0.0835, Cu(2) −0.0605]

Plane (2): N(1), N(2), N(5), O(1)

$$-0.2907X - 0.6363Y - 0.7146Z + 1.7164 = 0$$

[N(1) −0.020, N(2) 0.017, N(5) −0.014, O(1) 0.018, Cu(1) 0.0348, C(1) −0.017, C(2) −0.033, C(3) −0.277, C(4) −0.284, O(2) −0.015, O(3) −0.519]

Plane (3): N(3), N(4), N(6), O(4)

$$-0.3515X - 0.6798Y - 0.6437Z + 1.7670 = 0$$

[N(3) 0.027, N(4) −0.023, N(6) 0.021, O(4) −0.024, Cu(2) −0.0854, C(5) −0.027, C(6) −0.004, C(7) 0.321, C(8) 0.337, O(5) −0.053, O(6) 0.607]

Dihedral angles (°) between least-squares planes: (1)—(2) 5.8; (1)—(3) 10.4; (2)—(3) 5.9.

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Cu(1)–N(1)	1.891(3)	N(1)–C(2)	1.441(5)
Cu(2)–N(3)	1.896(3)	N(3)–C(6)	1.445(5)
Cu(1)–N(2)	2.021(4)	C(1)–C(2)	1.522(6)
Cu(2)–N(4)	2.036(3)	C(5)–C(6)	1.518(5)
Cu(1)–O(1)	2.004(3)	C(1)–O(1)	1.272(5)
Cu(2)–O(4)	2.000(3)	C(5)–O(4)	1.281(4)
Cu(1)–N(5)	1.928(3)	C(1)–O(2)	1.244(5)
Cu(2)–N(6)	1.940(3)	C(5)–O(5)	1.243(5)
N(2)–C(4)	1.485(6)	N(5)–C(9)	1.331(5)
N(4)–C(8)	1.482(5)	N(6)–C(9)	1.331(5)
C(3)–C(4)	1.506(6)	N(5)–C(10)	1.372(5)
C(7)–C(8)	1.521(5)	N(6)–C(11)	1.375(5)
N(1)–C(3)	1.306(5)	C(10)–C(11)	1.349(6)
N(3)–C(7)	1.288(5)	Cu(1) · · · Cu(2)	5.800(1)
C(3)–O(3)	1.257(5)		
C(7)–O(6)	1.262(5)		

(*b*) Angles

N(1)–Cu(1)–N(2)	83.26(14)	N(1)–C(2)–C(1)	108.6(3)
N(3)–Cu(2)–N(4)	83.29(13)	N(3)–C(6)–C(5)	108.6(3)
N(1)–Cu(1)–O(1)	82.90(12)	O(1)–C(1)–C(2)	117.5(3)
N(3)–Cu(2)–O(4)	82.48(13)	O(4)–C(5)–C(6)	117.0(3)
N(2)–Cu(1)–N(5)	99.08(14)	Cu(1)–O(1)–C(1)	114.5(3)
N(4)–Cu(2)–N(6)	99.34(13)	Cu(2)–O(4)–C(5)	115.0(2)
Cu(1)–N(5)–C(9)	124.5(3)	O(3)–C(3)–C(4)	119.4(4)
Cu(2)–N(6)–C(9)	124.1(3)	O(6)–C(7)–C(8)	118.2(3)
Cu(1)–N(5)–C(10)	131.2(3)	O(3)–C(3)–N(1)	126.5(4)
Cu(2)–N(6)–C(11)	131.3(3)	O(6)–C(7)–N(3)	127.4(4)
Cu(1)–N(2)–C(4)	109.4(3)	O(2)–C(1)–C(2)	118.6(4)
Cu(2)–N(4)–C(8)	108.9(2)	O(5)–C(5)–C(6)	119.5(3)
N(2)–C(4)–C(3)	112.0(3)	O(1)–C(1)–O(2)	124.0(4)
N(4)–C(8)–C(7)	112.0(3)	O(4)–C(5)–O(5)	123.5(3)
N(1)–C(3)–C(4)	114.1(3)	N(5)–C(9)–N(6)	113.7(3)
N(3)–C(7)–C(8)	114.4(3)	C(9)–N(5)–C(10)	104.3(3)
Cu(1)–N(1)–C(3)	119.7(3)	C(9)–N(6)–C(11)	104.7(3)
Cu(2)–N(3)–C(7)	119.8(3)	N(5)–C(10)–C(11)	109.1(4)
Cu(1)–N(1)–C(2)	116.5(2)	N(6)–C(11)–C(10)	108.3(4)
Cu(2)–N(3)–C(6)	116.7(2)		

(*c*) Possible hydrogen bonds *

N(2) · · · O(13$^{\mathrm{VII}}$)	2.984(9)	O(10) · · · O(9$^{\mathrm{I}}$)	2.754(5)
N(2) · · · O(9$^{\mathrm{VII}}$)	2.913(5)	O(10) · · · O(2$^{\mathrm{VI}}$)	2.838(5)
N(4) · · · O(2$^{\mathrm{IV}}$)	3.165(5)	O(11) · · · O(1$^{\mathrm{VI}}$)	2.902(4)
N(4) · · · O(11$^{\mathrm{IX}}$)	3.027(5)	O(11) · · · O(4$^{\mathrm{VI}}$)	2.779(4)
O(7) · · · O(6$^{\mathrm{VIII}}$)	2.760(5)	O(12) · · · O(10$^{\mathrm{VI}}$)	2.614(11)
O(7) · · · O(8$^{\mathrm{I}}$)	2.978(6)	O(12) · · · O(8$^{\mathrm{I}}$)	2.810(11)
O(8) · · · O(3$^{\mathrm{III}}$)	2.853(4)	O(12) · · · O(13$^{\mathrm{VI}}$)	2.881(13)
O(8) · · · O(2$^{\mathrm{VI}}$)	3.008(5)	O(13) · · · O(8$^{\mathrm{I}}$)	2.891(9)
O(9) · · · O(3$^{\mathrm{III}}$)	2.744(4)	O(13) · · · O(10$^{\mathrm{VI}}$)	2.980(9)
O(9) · · · O(6$^{\mathrm{II}}$)	2.723(4)		

(*d*) Short contacts *

Cu(1) · · · O(6$^{\mathrm{V}}$)	3.186(3)	Na$^+$ · · · O(5$^{\mathrm{VI}}$)	2.406(3)
Cu(2) · · · O(3$^{\mathrm{VII}}$)	2.723(3)	Na$^+$ · · · O(5$^{\mathrm{II}}$)	2.313(3)
		Na$^+$ · · · O(7$^{\mathrm{II}}$)	2.374(4)
		Na$^+$ · · · O(11$^{\mathrm{I}}$)	2.332(3)
		Na$^+$ · · · O(12$^{\mathrm{VI}}$)	2.899(10)

* Roman numeral superscripts refer to atoms in the positions: I *x*, *y*, *z*; II *x*, $1 + y$, *z*; III $1 + x$, *y*, $1 + z$; IV *x*, *y*, $1 + z$; V $-x$, $-y$, $-z$; VI $1 - x$, $1 - y$, $-z$; VII $-x$, $1 - y$, $-z$; VIII $1 - x$, *y*, $1 - z$; IX $-1 + x$, $-1 + y$, *z*.

the literature.[9-12] The imidazolate ring is flattened with the C(9)–N(5)–C(10) and C(9)–N(6)–C(11) angles smaller and the N(5)–C(9)–N(6) angle larger than 108°. This type of flattening is typical for bridging imidazolate ligands.[9-11] The other bond distances and angles are normal (Table 3).

The structure (Figure 2) consists of discrete binuclear [Cu$_2$(Gly-GlyO)$_2$(im)]$^-$ units, sodium ions, and water molecules of crystallization. The complex anions, which are mutually connected by weak Cu–O co-ordinate bonds, Na$^+$ · · · O(carboxylate and water) electrostatic forces, and hydrogen bonds, are disposed along the *b* axis. The rows of the complexes along the *b* axis are connected mainly by the hydrogen bonds. The '*cis*' structure of the complex anion is fixed by many hydrogen bonds and $Na^+ \cdots O$(caboxylate) electrostatic forces. Hydrogen bonds and short contact distances are summarized in Table 3.

Magnetism.—The antiferromagnetic exchange interaction of the imidazolate-bridged binuclear copper(II) complexes is of interest in connection with the structure of the active site of bovine erythrocyte superoxide dismutase. Dewan and Lippard[9] showed that the dihedral angles between the imidazolate ring and the copper(II) co-ordination planes are 4.69 and 13.37° in $[Cu_2(bpim)]^{3+}$ (bpim = 4,5-bis{[2′-(2″-pyridyl)ethylimino]methyl}-imidazolyl) and the coupling constant J is -81.3 cm^{-1},[13] while in $[Cu_2(ppy)_2(im)]^{3+}$ (ppy = 2-{[2′-(2″-pyridyl)-ethylimino]methyl}pyridine) the angle is 88.88° and the coupling constant J is $-$ 26.74 cm^{-1}.[13] The J values appear to be a function of the dihedral angles between the bridging imidazolate and the copper(II) co-ordination planes.[9,13] The present complex, however, shows a small J value (-19 cm^{-1}) despite the coplanar disposition of the imidazolate and the two copper(II) co-ordination planes, indicating that the J value seems to be independent of the dihedral angles. Thus, the dihedral angles are not expected to be close to 90° in $4Cu^{2+}$–bovine erythrocyte superoxide dismutase ($J = -26$ cm^{-1})[14] in which Cu^{II} replaces the Zn^{II} present in the native enzyme.

Haddad and Hendrickson[15] demonstrated that in the series $[Cu_2(tren)_2(L)]^{n+}$ (tren = 2,2′,2″-triaminotriethylamine, L = bridging ligand), the interaction decreases in the order of L = 2-Me-im$^-$(2-Me-im$^-$ = 2-methylimidazolyl, $J = -49$ cm^{-1}), im ($J = -38$ cm^{-1}), bzim$^-$ (bzim$^-$ = benzimidazolyl, $J = -24$ cm^{-1}), and bim^{2-} (bim^{2-} = bi-imidazolyl, $|J| < 0.5$ cm^{-1}). The extent of the overlap of the Cu d_{z^2} orbitals with the σ molecular orbitals of bridging ligands seems to be an important factor in determining the J value.[15] Increasing the Cu–N(imidazolate)–C(imidazolate) angle (α) in going from bim^{2-} to 2-Me-im$^-$ could lead to a more favourable situation for the overlap.[15]

On the other hand, Dewan and Lippard[9] recently indicated that the difference in angle (θ) between the Cu–N(imidazolate) vectors, and not the dihedral angle differences, is the more important factor in determining J.

In Table 4 the structural parameters which appear to be responsible for the coupling constant are listed for several complexes. Comparison of the numerical data in Table 4 shows that the larger the spin–spin magnetic interaction is, the larger the values of α and θ are. Both the Cu–N(imidazolate)–C(imidazolate) angle (α) and the angle (θ) between the Cu–N(imidazolate) vectors thus play an important role in the spin–spin magnetic interaction in the imidazolate-bridged binuclear copper(II) complexes. The α and θ values in $4Cu^{2+}$–bovine erythrocyte superoxide dismutase are supposed to be similar to those in $[Cu_2(tmdt)_2(im)(ClO_4)_2][ClO_4]$ (tmdt = *NNN″N″*-tetramethyldiethylenetriamine) because of their similar J values.

TABLE 4

Values of the Cu–N(imidazolate)–C(imidazolate) angle (α), the angle between the Cu–N(imidazolate) vectors (θ), and the coupling constant J for several complexes

$[Cu_2(bpim)(NO_3)_2(ClO_4)(OH_2)]\cdot H_2O$ [a]
$\alpha = 143°, \theta = 170°, J = -81.3$ cm^{-1}
$[Cu_2(tmdt)_2(im)(ClO_4)_2][ClO_4]$ [b]
$\alpha = 129°, \theta = 143°, J = -25.8$ cm^{-1}
$Na[Cu_2(Gly\text{-}GlyO)_2(im)]\cdot 6H_2O$ [c]
$\alpha = 124°, \theta = 135°, J = -19$ cm^{-1}
$[Cu_2(pmdt)_2(bim)][BPh_4]_2$ [d]
$\alpha = 112°, \theta = 97°, |J| < 0.5$ cm^{-1}

[a] Refs. 9 and 13. [b] Ref. 10. [c] Ref. 2. [d] Refs. 11 and 15; pmdt = *NNN′N″N″*-pentamethyldiethylenetriamine.

The Cu–N(imidazolate) bond distance of 1.934(3) Å in the present complex is smaller than those [1.964(7),[9] 1.955(14),[10] 1.993(3) and 2.324(3),[11] and 1.968 Å[12]] previously reported. Since the magnitude of the observed coupling constant (J) (Table 4) is not reflected in the Cu–N(imidazolate) bond distance, the Cu–N(imidazolate) bond distance is less important in determining the magnitude of the spin–spin magnetic interaction.

The coupling constant of an imidazolate-bridged dicopper(II) complex showing a large spin–spin magnetic interaction is found to be *ca.* -90 cm^{-1} at best. The interaction between the two copper(II) ions in such a complex is much smaller than that between type III coppers which exhibit extremely strong antiferromagnetic interaction. These observations suggest that the imidazolate-bridged dicopper(II) structure (Cu–im–Cu) cannot be expected to be involved in proteins having type III coppers.

[1/225 *Received, 11th February*, 1981]

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