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Molecular Structure of Imidazolate-Bridged Binuclear Zinc Complex and Its Single-Crystal ESR Spectra Doped with Bridged Cu–Zn Complex

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The X-ray crystal structure of $[(dtma)ZnImZn(dtma)]ClO_4\cdot 2.5H_2O$ (dtmaH = 4-diethylenetriamineacetic acid) was determined. The crystals are orthorhombic, space group *Pbcn*, with $a = 14.104(5)$, $b = 14.897(5)$, $c = 25.384(9)$ Å, and $Z = 8$. Least-squares refinement of the structure leads to a conventional R factor of 0.066. The magnetic properties of $[(dtma)ZnImCu(dtma)]ClO_4\cdot 2.5H_2O$ are investigated. From the single-crystal ESR spectra of Zn–Im–Zn dimer doped with Zn–Im–Cu complex, the anisotropic **g** and **A** tensors of Cu–Zn complex are obtained, and the bonding nature of Cu is discussed.

Introduction

Discrete imidazolate-bridged polynuclear complexes have attracted much attention since an imidazolate-bridged copper–zinc center was discovered in bovine erythrocyte superoxide dismutase.[1,2] These compounds provide adequate model systems for the enzyme in some cases, and the study of them is helpful to understand the relationship of enzyme's structure and function.[3,4] However, the complexes having an imidazolate bridge between copper and zinc are difficult to synthesize. Only recently, the syntheses of $[(dtma)ZnImCu(dtma)]ClO_4$ and $[(tren)ZnImCu(tren)](ClO_4)_3$ and the determination of their crystal structures have been reported by us.[5,6] In order to elucidate the electronic structure and bonding nature of Cu^{2+} in Zn–Im–Cu complexes, we herein report the ESR studies of $[(dtma)ZnImCu(dtma)]ClO_4\cdot 2.5H_2O$ doped in single crystals of the corresponding Zn–Im–Zn complex and the structure of the latter.

Experimental Section

Preparation. The ligand dtmaH and its coordination compounds $[Zn(dtma)]ClO_4$ and $[(dtma)ZnImCu(dtma)]ClO_4\cdot 2.5H_2O$ were prepared as described in the literature.[5,7] Other compounds were prepared as follows:

$[Zn(dtma)ImH]ClO_4\cdot 1.5H_2O$. To a solution containing 0.325 g (1 mmol) of $[Zn(dtma)ClO_4$ in 10 mL of water was added 0.075 g (1.1 mmol) of imidazole (ImH). After being stirred for 5 min, the solution was filtered and the filtrate was concentrated at room temperature in vacuum. Colorless crystals were collected, washed with water and ethanol, and recrystallized in water. Yield 69%. Anal. Found: C, 25.8; H, 4.7; N, 17.0; Zn, 15.5. Calcd for $C_9H_{21}N_5ClO_{7.5}Zn$: C, 25.7; H, 5.0; N, 16.7; Zn, 15.6.

$[(dtma)ZnImZn(dtma)]ClO_4\cdot 2.5H_2O$. $[Zn(dtma)ImH]ClO_4\cdot 1.5H_2O$ [0.420 g (1 mmol)] and $[Zn(dtma)]ClO_4$ [0.325 g (1 mmol)] were mixed in water (15 mL), and then NaOH solution (1.0 mL, 1.0 N) was added when stirring. After filtration, evaporation under vacuum, and washing with water, colorless crystals were obtained. Anal. Found: C, 27.7; H, 5.3; N, 17.0; Zn, 20.0. Calcd for $C_{15}H_{36}N_8ClO_{10.5}Zn_2$: C, 27.2; H, 5.5; N, 16.9; Zn, 19.7.

Table I. Crystal Data for the Title Complex

formula	$C_{15}H_{36}N_8ClO_{10.5}Zn_2$
formular weight	662.71
space group	*Pbcn*
a (Å)	14.104(5)
b (Å)	14.897(5)
c (Å)	25.384(9)
Z	8
V (Å^3)	5339(3)
$F(000)$	2736
d_c (g cm^{-3})	1.651
crystal size (mm)	0.7 × 0.6 × 0.4
$\mu(MoK_\alpha)$ (cm^{-1})	20.06
radiation (MoK_α, Å)	0.71069
orientation reflections number	25
range	$6.9° < 2\theta < 17.9°$
data collection range	$1° < 2\theta < 43°$
number of unique data	3562
total with $I > 1.5\sigma$	2450
R^a	0.066
$R_w{}^b$	0.066

[a] $R = \sum|F_o - F_c|/\sum F_o$. [b] $R_w = \sum[|F_o - F_c|w^{1/2}]/\sum[|F_o|w^{1/2}] w = 1/[\sigma^2(F) + |g|F^2]$.

Mixed Single-Crystal Samples. Single crystals of Zn–Im–Cu and Zn–Im–Zn mixture were grown at room temperature by slow evaporation of an aqueous solution mixture of $[(dtma)ZnImCu(dtma)]ClO_4\cdot 2.5H_2O$ and $[(dtma)ZnImZn(dtma)]ClO_4\cdot 2.5H_2O$ in a molar ratio of 1:12. The magnetically diluted blue Zn–Im–Cu crystal was found with a well-developed (001) face. The maximum value of the d–d electronic transitions obtained from powder reflectance spectroscopy for Cu^{2+} in the mixed crystal is 700 nm, which is in agreement with the value for pure $[(dtma)ZnImCu(dtma)]ClO_4\cdot 2.5H_2O$. It indicates that Zn–Im–Zn crystal is doped with Cu^{2+} in the form of Zn–Im–Cu.

X-ray Crystallography. Cell dimensions were determined on R3M/E four-circle diffractometer, and reflection intensities were measured in the $\omega - 2\theta$ scan mode with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Intensities were not corrected for absorption. The atomic coordinates of the metal atoms were first obtained by analyzing Patterson functions. The other non-H atom coordinates were gradually obtained by Fourier synthesis. After all the coordinates and isotropic and anisotropic thermal parameters of non-H atoms were refined, the hydrogen atom coordinates were obtained from difference Fourier synthesis and analysis of geometry. Finally, the coordinates, the anisotropic thermal parameters of non-H atoms, and the isotropic thermal parameters of H atoms were refined by the block diagonal matrix least-squares method. All calculations were performed on a PDP 11/44 computer with the SDP program system.[8] Crystal data, atomic parameters and temperature factors, and selected bond distances and angle data are given in Tables I–III, respectively, all of which indicate that Zn–Im–Zn is isomorphous

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Table II. Atomic Coordination and Thermal Parameters of Zn–Im–Zn

	x	*y*	*z*	*U* (Å^2)
Zn(1)	2276(1)	7050(1)	6773(1)	34(1)^a
Zn(2)	2538(1)	10073(1)	8361(1)	38(1)^a
Cl	4569(2)	8215(2)	5542(2)	81(1)^a
N(1)	2046(6)	6178(5)	6047(3)	42(3)^a
N(2)	1094(6)	6376(6)	7049(3)	50(3)^a
N(3)	1993(7)	8028(5)	6193(3)	47(3)^a
N(4)	2802(5)	7916(5)	7311(3)	42(5)^a
N(5)	2909(6)	9045(5)	7884(3)	39(3)^a
N(6)	2707(8)	9484(6)	9096(3)	60(4)^a
N(7)	1251(6)	10478(6)	8021(4)	51(3)^a
N(8)	2237(7)	11263(6)	8896(4)	56(4)^a
O(1)	3906(6)	4804(5)	6613(4)	69(3)^a
O(2)	3308(5)	6097(4)	6887(3)	47(3)^a
O(3)	3636(5)	10916(4)	8174(3)	46(3)^a
O(4)	4344(6)	12212(5)	8333(4)	70(3)^a
O(5)	3738(8)	8603(8)	5449(6)	141(7)^a
O(6)	4390(11)	7493(17)	5832(11)	361(18)^a
O(7)	5238(10)	8696(10)	5736(9)	222(11)^a
O(8)	4850(15)	7860(16)	5116(9)	304(15)^a
Ow(1)	9427(9)	1101(7)	1222(5)	118(6)^a
Ow(2)	9414(15)	918(13)	153(7)	249(12)^a
Ow(3)	0	1129(19)	2500	504(43)^a
C(1)	2869(9)	5559(7)	6031(4)	59(5)^a
C(2)	3393(8)	5461(6)	6549(4)	46(4)^a
C(3)	1134(9)	5726(8)	6158(4)	56(4)^a
C(4)	1035(9)	5533(8)	6740(5)	65(5)^a
C(5)	1954(9)	6764(7)	5583(4)	56(4)^a
C(6)	1479(9)	7633(7)	5744(4)	58(5)^a
C(7)	3751(7)	8096(7)	7399(4)	45(4)^a
C(8)	3818(7)	8778(7)	7746(4)	44(4)^a
C(9)	2349(8)	8504(7)	7609(4)	48(4)^a
C(10)	3726(9)	11665(7)	8420(5)	55(4)^a
C(11)	3057(13)	11872(8)	8861(6)	120(8)^a
C(12)	2789(12)	10160(8)	9520(4)	89(7)^a
C(13)	2114(11)	10907(9)	9426(5)	74(6)^a
C(14)	840(8)	11201(8)	8347(7)	96(7)^a
C(15)	1387(16)	11623(15)	8694(10)	211(14)^a

[a] Equivalent isotropic *U* defined as one-third of the trace f the orthogonalized $U_{i,j}$ tensor.

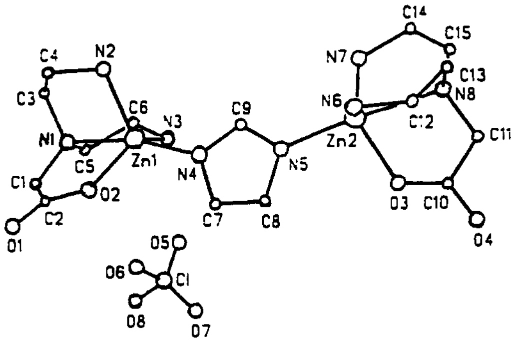

Figure 1. Molecular structure of [(dtma)ZnImZn(dtma)]ClO$_4$.

with Zn–Im–Cu and both belong to an orthorhombic system, space group *Pbcn*, and have similar crystallographic parameters.[5] The structure is shown in Figure 1.

Single-Crystal ESR Spectra. The ESR spectra were recorded with a Bruker ER200D-SRC X-band spectrometer. A crystal with size of 1 × 2.5 × 1.5 mm was chosen, and the experimental frame was selected so that the *x*, *y*, and *z* axes parallelled *c*, *a*, and *b* axes of the crystal unit cell, respectively, as shown in Figure 2. ESR spectra for magnetic field orientations at the three orthogonal planes about 5° intervals are recorded.

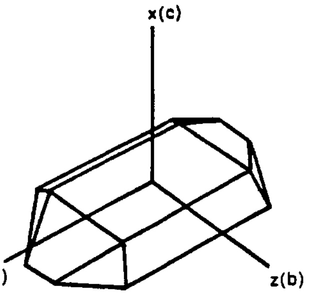

Figure 2. Growth morphology, experimental frame (*x*, *y*, *z*), and orientations of the crystallographic axes for the ideal mixed single crystal.

Table III. Selected Bond Distances and Angles for Zn–Im–Zn

(a) Bond Lengths (Å)

Zn(1)–N(1)	2.278(8)	Zn(1)–N(2)	2.067(9)
Zn(1)–N(3)	2.111(8)	Zn(1)–N(4)	2.020(8)
Zn(1)–O(2)	2.054(7)	Zn(2)–N(5)	2.022(8)
Zn(2)–N(6)	2.077(9)	Zn(2)–N(7)	2.098(9)
Zn(2)–N(8)	2.273(9)	Zn(2)–O(3)	2.049(7)
Cl–O(5)	1.329(12)	Cl–O(6)	1.328(26)
Cl–O(7)	1.283(16)	Cl–O(8)	1.266(23)
N(1)–C(1)	1.492(14)	N(1)–C(3)	1.479(15)
N(1)–C(5)	1.472(13)	N(2)–C(4)	1.483(15)
N(3)–C(6)	1.473(14)	N(4)–C(7)	1.383(12)
N(4)–C(9)	1.322(13)	N(5)–C(8)	1.387(13)
N(5)–C(9)	1.328(13)	N(6)–C(12)	1.477(15)
N(7)–C(14)	1.477(17)	N(8)–C(11)	1.473(19)
N(8)–C(13)	1.457(15)	N(8)–C(15)	1.409(25)
O(1)–C(2)	1.228(13)	O(2)–C(2)	1.285(12)
O(3)–C(10)	1.285(13)	O(4)–C(10)	1.213(15)
C(1)–C(2)	1.515(16)	C(3)–C(4)	1.511(17)
C(5)–C(6)	1.513(16)	C(7)–C(8)	1.347(15)
C(10)–C(11)	1.496(21)	C(12)–C(13)	1.484(20)
C(14)–C(15)	1.329(27)		

(b) Bond Angles (deg)

N(1)–Zn(1)–N(2)	83.2(3)	N(1)–Zn(1)–N(3)	78.6(3)
N(2)–Zn(1)–N(3)	114.8(3)	N(1)–Zn(1)–N(4)	164.4(3)
N(2)–Zn(1)–N(4)	112.2(3)	N(3)–Zn(1)–N(4)	95.7(3)
N(1)–Zn(1)–O(2)	79.7(3)	N(2)–Zn(1)–O(2)	100.9(3)
N(3)–Zn(1)–O(2)	135.2(3)	N(4)–Zn(1)–O(2)	94.9(3)
N(5)–Zn(2)–N(6)	100.9(3)	N(5)–Zn(2)–N(7)	101.3(3)
N(6)–Zn(2)–N(7)	126.2(4)	N(5)–Zn(2)–N(8)	175.6(3)
N(6)–Zn(2)–N(8)	79.3(3)	N(7)–Zn(2)–N(8)	82.0(3)
N(5)–Zn(2)–O(3)	97.5(3)	N(6)–Zn(2)–O(3)	112.3(4)
N(7)–Zn(2)–O(3)	112.5(3)	N(8)–Zn(2)–O(3)	78.5(3)
O(5)–Cl–O(6)	106.4(9)	O(5)–Cl–O(7)	118.3(9)
O(6)–Cl–O(7)	112.3(14)	O(5)–Cl–O(8)	107.8(12)
O(6)–Cl–O(8)	101.3(16)	O(7)–Cl–O(8)	109.3(14)
Zn(1)–N(1)–C(1)	105.7(6)	Zn(1)–N(1)–C(3)	103.2(6)
C(1)–N(1)–C(3)	113.3(8)	Zn(1)–N(1)–C(5)	108.8(6)
C(1)–N(1)–C(5)	114.8(8)	Zn(3)–N(1)–C(5)	110.2(9)
Zn(1)–N(2)–C(4)	106.1(7)	Zn(1)–N(3)–C(6)	110.9(6)
Zn(1)–N(4)–C(7)	126.1(7)	Zn(1)–N(4)–C(9)	129.2(7)
C(7)–N(4)–C(9)	104.3(8)	Zn(2)–N(5)–C(8)	127.4(7)
Zn(2)–N(5)–C(9)	128.3(7)	C(8)–N(5)–C(9)	104.1(8)
Zn(2)–N(6)–C(12)	112.1(7)	Zn(2)–N(7)–C(14)	108.5(8)
Zn(2)–N(8)–C(11)	107.4(8)	Zn(2)–N(8)–C(13)	106.8(7)
C(11)–N(8)–C(13)	111.9(10)	Zn(2)–N(8)–C(15)	103.8(11)
C(11)–N(8)–C(15)	114.3(12)	C(13)–N(8)–C(15)	111.9(13)
Zn(1)–O(2)–C(2)	118.8(7)	Zn(2)–O(3)–C(10)	119.7(7)
N(1)–C(1)–C(2)	114.2(9)	O(1)–C(2)–O(2)	123.7(10)
O(1)–C(2)–C(1)	118.1(10)	O(2)–C(2)–C(1)	118.1(9)
N(1)–C(3)–C(4)	110.7(9)	N(2)–C(4)–C(3)	110.5(9)
N(1)–C(5)–C(6)	109.3(8)	N(3)–C(6)–C(5)	109.5(9)
N(4)–C(7)–C(8)	108.7(9)	N(5)–C(8)–C(7)	108.4(9)
N(4)–C(9)–N(5)	114.5(9)	O(3)–C(10)–O(4)	124.5(11)
O(3)–C(10)–C(11)	118.7(11)	O(4)–C(10)–O(11)	116.8(11)
N(8)–C(11)–C(10)	114.4(11)	N(6)–C(12)–O(13)	110.0(11)
N(8)–C(13)–C(12)	110.2(10)	N(7)–C(14)–C(15)	119.3(13)
N(8)–C(15)–C(14)	123.6(18)		

Results and Discussion

Description of Structure. The Zn–Im–Zn compound consists of a [(dtma)ZnImZn(dtma)]$^+$ cation, a ClO$_4^-$ anion, and two and one-half water molecules. In the cation, two Zn atoms are bridged by a imidazolate anion (Im$^-$), forming a binuclear complex. Each of the two Zn atoms is pentacoordinated by one O and three N atoms from dtma and one N atom from the bridging imidazolate ion in an approximately trigonal bipyramidal structure with N(2), N(3), O(2) and N(6), N(7), O(3) atoms forming the trigonal planes and N(1), N(4) and N(8), N(5) atoms at the apexes separately. The degree of distortion (Δ) from trigonal

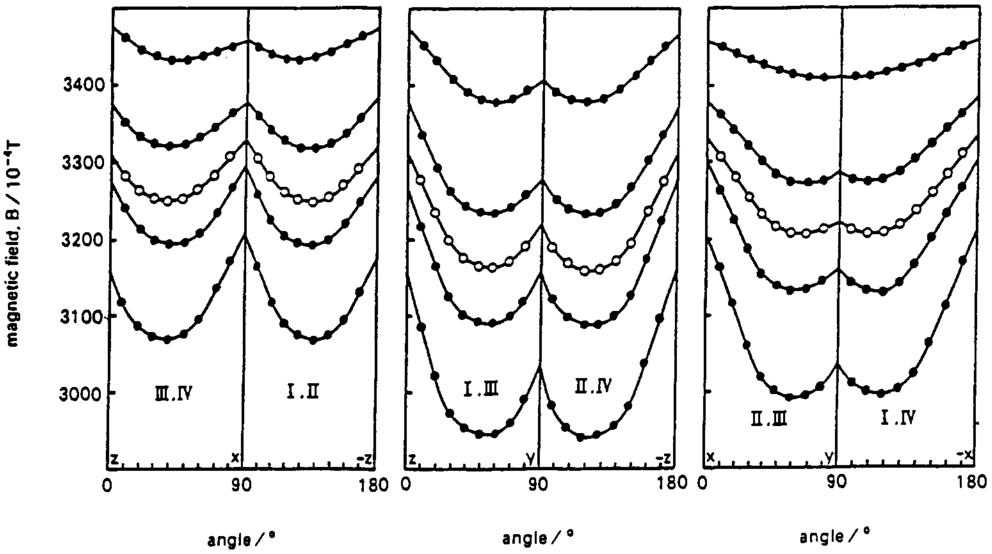

Figure 3. Angular variation of the ESR spectra for the magnetic field lying in the *zx*, *zy*, and *xy* planes. (●) Experimental data for hyperfine lines. (○) Central points of the hyperfine lines. (—) Calculated positions.

bipyramid (TBP) to square pyramid (SP) can be estimated according to Muetterties and Galy.[9,10] In the ideal TBP, $\Delta = 0$, and in the ideal SP, $\Delta = 1$. The fact that the values of Δ are 0.53 and 0.08 for Zn(1) and Zn(2), respectively, indicates the geometry of coordination around the Zn(1) is just intermediate between TBP and SP and that around the Zn(2) is very close to TBP.

The average bond lengths of Zn(1)–N and Zn(2)–N are 2.119(9) and 2.117(9) Å, respectively. All the Zn–O bond lengths are 2.05 Å. The distance between two Zn atoms is 6.06 Å. All these parameters are close to the values of corresponding bond lengths and distances of the Zn–Im–Cu complex.[5]

The bond distances of N–C and C–C in the imidazolate anion group range from 1.319 to 1.372 Å and the bond angles from 104.1° to 113.2°, which are close to the respective values in other imidazolate-bridged compounds.[5,11] The imidazolate anion shows good planar conformation.

Analysis of the ESR Data. If in the mixed single crystal the Cu ion always occupies one of the two crystallographically distinct sites in the Zn–Im–Zn molecule, for the orthorhombic crystal, four magnetically nonequivalent sites in the cell are expected, but in the crystallographic principal planes *bc*, *ba*, and *ca* (i.e., *zx*, *zy*, and *xy*) they are generally degenerate in pairs and only two sets of hyperfine lines are recorded for a general orientation of the static magnetic field in these planes.[12] The angular variations of the single-crystal ESR of the complex for the magnetic field lying in the *zx*, *zy*, and *xy* planes in turn are shown in Figure 3. As seen in Figure 3, in the *zx* plane only the signals of sites III and IV are in the range *x* to *z*, and those of sites I and II are in the range *x* to −*z*. This reason is that the signals of sites III and IV in the range *x* to −*z* and those of sites I and II in the range *x* to *z* are not resolved well. A similar situation happens in *zy* and *xy* planes. Fortunately, there are reversal points of hyperfine lines on the principal axes, so we can reasonably consider that the signals shown in the 0–90° and 90–180° ranges are two different ones, which are from different magnetically nonequivalent sites. The principal values of the g and A tensors and their directions were calculated using the least-squares fitting procedure.[13] In fitting there are two groups of different principal g tensors, one group of which yields reasonable the principal A tensors. When checking them with the polycrystalline powder spectra, where $g_{\parallel}$ and $A_{\parallel}$ are 2.236 and 162 × 10^{-4} cm^{-1}, respectively, we found that the two results are extremely consistent with each other. The principal values obtained of g and A tensors and their directions for four nonequivalent sites are shown in Table IV. It is seen in Table IV that the principal values of the g and A tensors for the four sites are reasonably consistent, and the direction cosines of the principal axes of the g and A tensors for the four sites do reveal the orientations of four magnetically nonequivalent but geometrically identical Cu(II) ions in a unit cell. In addition, the angle between g_{zz} and A_{zz} directions is ca. 1.8°, which indicates the g_{zz} and A_{zz} directions basically coincide in this copper(II) complex. All these results support the assumption that Cu ion occupies one site in the Zn–Im–Zn molecule.

Table IV. Spin-Hamiltonian Parameters of Cu(II) for the Mixed Single Crystal

site	principal values		direction cosines of the principal axes		
			x^a	y	z
I	g_{xx}	2.048	−0.5249	0.3048	−0.7947
	g_{yy}	2.084	0.7509	0.6055	−0.2636
	g_{zz}	2.240	−0.4009	0.7351	0.5467
	$A_{xx}{}^b$	25.00	−0.8516	−0.0419	−0.5226
	A_{yy}	43.02	0.3536	0.6885	−0.6332
	A_{zz}	166.6	−0.4282	0.7209	0.5448
II	g_{xx}	2.047	0.5317	0.3013	0.7915
	g_{yy}	2.083	0.7455	−0.6099	−0.2686
	g_{zz}	2.240	−0.4018	−0.7329	0.5489
	A_{xx}	24.86	0.8330	−0.0808	0.5473
	A_{yy}	43.06	0.3506	−0.6887	−0.6335
	A_{zz}	166.6	−0.4278	−0.7213	0.5446
III	g_{xx}	2.048	0.5406	0.2902	−0.7896
	g_{yy}	2.084	0.7396	−0.6111	0.2818
	g_{zz}	2.240	0.4008	0.7364	0.5450
	A_{xx}	25.02	0.8744	−0.1843	−0.4489
	A_{yy}	43.22	0.2239	−0.6673	0.7102
	A_{zz}	166.8	0.4304	0.7215	0.5422
IV	g_{xx}	2.048	−0.5274	0.3027	0.7938
	g_{yy}	2.084	0.7490	0.6066	0.2663
	g_{zz}	2.240	0.4010	−0.7351	0.5467
	A_{xx}	25.25	−0.8767	−0.1910	0.4415
	A_{yy}	42.79	0.2148	0.6657	0.7145
	A_{zz}	166.8	0.4305	−0.7214	0.5426

[a] (x, y, z) is the experimental frame defined in Figure 2. [b] Unit of the A is 10^{-4} cm^{-1}.

The Cu/Zn atoms in the structure of the Zn–Im–Cu complex are not disordered or switched over. It was found that when the Cu/Zn positions in the molecule were exchanged, after final

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refinement the R value became larger than that in the original,[5] and the Zn(1) position in Zn(1)–Im–Zn(2) complex corresponds to the Zn position in the Zn–Im–Cu complex, which is about 4 Å away from the Cl of ClO_4^-, and the Zn(2) position corresponds to the Cu position, which is about 8 Å away. Therefore, we can suppose that, in the crystals of Zm–Im–Cu complex which was mixed with Zn(1)–Im–Zn(2), the Cu should keep its position as in the structure of the Zn–Im–Cu molecule and occupy the Zn(2) site in the mixed crystal.

The angular dependence of the expression of **g** and **A** tensors for five-coordinate Cu(II) complexes possessing geometries intermediate between the two limiting forms, square pyramid and trigonal bipyramid, have been calculated by Florence group using an angular overlap approach.[14] The criteria suggested by them are as follows: g_{zz} ($\approx$2.27) $\gg g_{yy} \geq g_{xx}$ ($\approx$2.07), and $|A_{zz}|$ ($\approx 150 \times 10^{-4}$ cm^{-1}) $\gg |A_{yy}| \approx A_{xx}$ (20×10^{-4} cm^{-1}) for square pyramidal Cu(II) complexes with ground state $d_{x^2-y^2}$; g_{zz} ($\approx$2.22) $\approx g_{yy} \gg g_{xx}$ ($\approx$2.00), $|A_{zz}|$ (70×10^{-4} cm^{-1}) $\approx |A_{yy}| \geq A_{xx}$ (60×10^{-4} cm^{-1}) for trigonal bipyramidal complexes with d_{z^2} ground state;[14,15] and g_{yy} and A_{yy} are most highly affected by the variation of α.[14] For Cu(II)-doped Zn–Im–Zn complex g_{zz} (=2.24) is significantly greater than the free electron value, $|A_{zz}| = 166.6 \times 10^{-4}$ cm^{-1}, near to the value of 150×10^{-4} cm^{-1}, $g_{yy} \geq g_{xx}$, and $A_{xx} \geq A_{yy}$; all these indicate the local symmetry of the Cu(II) ion is near to square pyramidal with mainly $d_{x^2-y^2}$ ground state.

In order to further evaluate the distortion of local symmetry for Cu(II) doped in Zn–Im–Zn complex from square pyramidal geometry semiquantitatively, the mixing coefficient of c for the Cu(II) are calculated according to the vibronic coupling model advanced by D. Reinen et al.[16,17] The ground-state wave function of a five-coordinate Cu(II) complex along the distortion coordinate for transition from TBP to SP configuration or to the reverse geometry is

$$\varphi_g = (1 + c^2)^{-1/2}(d_{z^2} + c d_{x^2-y^2}) \tag{1}$$

The mixing coefficient is $c = 0$ for the TBP (D_{3h}) with d_{z^2} ground state and $c = +3^{-1/2}$ or $c = -3^{-1/2}$ for the SP (C_{2v}) with a $d_{z^2-y^2}$ or $d_{z^2-x^2}$ ground state.[16] From the following equation:

$$g_z = g_0 + 8u_z\left(\frac{c^2}{1 + c^2}\right)$$

$$g_{x(y)} = g_0 + 2u_{x(y)}\left(\frac{c^2}{1 + c^2}\right)\left(1 \pm \frac{3^{1/2}}{c}\right)^2 \tag{2}$$

with

$$u_i = \frac{k_i{}^2\xi_0}{\Delta_i} \qquad i = x, y, z$$

$c = +0.48$ is obtained, which is close to but less than $3^{1/2}$. This indicates that the configuration of Cu(II) doped in Zn–Im–Zn complex is a distorted SP and the ground state is mainly near to $d_{z^2-y^2}$,[17] which corresponds to ground state of $d_{x^2-y^2}$ when the C_2 axis is defined as the z axis in a coordinate system. Therefore, this is consistent with the conclusions obtained for a simple model. In the above calculation, $k_i = 0.74$, $\xi_0 = 830$ cm^{-1}, $g_0 = 2.0023$, and $\Delta_i = 14\,300$ cm^{-1} are used[16] (values of Δ_i are obtained from the reflection spectrum of the Zn–Im–Cu complex). In addition, the substitutions $g_{xx} \rightarrow g_z$, $g_{yy} \rightarrow g_y$, and $g_{zz} \rightarrow g_x$ are performed in the calculation system defined by the C_3 axis as the g_{zz} direction and the C_2 axis as the g_{xx} direction, which is different from that defined by us.

Table V. Angles of **g Directions** with Bonds of CuN_4O Chromophores in the Zn(2) Site[a–c]

molecule	bond	site I			site II			site III			site IV		
		g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}	g_{xx}	g_{yy}	g_{zz}
1	Cu–O(2)	80	82	**12**	52	39	83	69	65	36	33	62	74
	Cu–N(1)	**6**	83	89	32	66	70	71	36	61	79	59	34
	Cu–N(2)	88	19	71	77	57	36	2	71	69	47	44	83
	Cu–N(3)	77	20	75	74	86	17	43	77	50	77	38	55
	Cu–N(4)	**6**	84	88	33	65	69	70	35	63	79	60	32
2	Cu–O(2)	67	64	36	33	62	74	80	83	**12**	52	39	83
	Cu–N(1)	70	36	61	79	59	33	**5**	84	89	32	66	70
	Cu–N(2)	29	70	69	47	44	83	87	19	71	77	57	37
	Cu–N(3)	43	77	50	77	38	55	78	19	75	73	86	17
	Cu–N(4)	69	35	63	79	60	32	**5**	85	88	33	65	69
3	Cu–O(2)	51	39	83	80	83	**12**	34	61	74	67	64	36
	Cu–N(1)	32	66	70	**6**	83	89	79	58	34	70	36	61
	Cu–N(2)	77	56	37	88	19	72	46	44	83	29	70	69
	Cu–N(3)	74	86	17	77	20	75	76	38	55	43	78	50
	Cu–N(4)	34	65	69	**5**	84	88	79	60	32	69	35	63
4	Cu–O(2)	33	62	74	67	64	36	53	38	83	80	83	**12**
	Cu–N(1)	78	58	34	70	36	61	31	67	70	**6**	83	89
	Cu–N(2)	48	43	83	29	71	69	76	57	37	88	19	71
	Cu–N(3)	77	38	85	43	77	50	74	86	17	77	20	75
	Cu–N(4)	79	60	32	70	35	62	34	66	69	**6**	84	88

[a] The structural data are taken from the X-ray structure of the Cu-Im-Zn complex from ref 5. [b] The positions of O(2), N(1), N(2), N(3) and N(4) in the Zn-Im-Cu molecule correspond to the positions of O(3), N(8), N(6), N(7), and N(5) in the Zn(1)-Im-Zn(2) molecule, respectively. [c] The error of calculation of each angle is ±1°. [d] The coordinates of equivalent positions of four molecules are as follows: x,y,z; $^1/_2-x$, $^1/_2-y$, $^1/_2+z$; $^1/_2+x$, $^1/_2-y,z$; and x,y, $^1/_2-z$ (in numerical order).

Since Cu(II) ions occupy Zn(2) sites in mixed crystals and the local symmetry of the Cu(II) ions distorted to square pyramid,[5] one can expect that the C_2 axis of the local C_{2v} symmetry might correspond to the Cu–O(2) direction in the Zn–Im–Cu complex or the Zn(2)–O(3) direction in the Zn(1)–Im–Zn(2) complex, and the pseudo C_3 axis, to the Cu–N(4) direction or the Zn–N(5) direction. Therefore, in the following we only need to assign the **g** and **A** tensors of four sites to four magnetically inequivalent Zn(2) positions.

The assignment of the principal axes of the **g** tensors of four sites to four magnetically inequivalent Cu(II) ion-doped Zn(2) sites is performed by comparison of direction cosines determined from ESR and the direction of Cu–O(2) (C_2 axis) and Cu–N(4) (pseudo C_3 axis) bonds with respect to the Zn(2) position for eight molecules in a unit cell in mixed crystals. All angles of the **g** directions of four sites with various Cu–N and Cu–O bonds of four CuN_4O chromophores in the Zn(2) site are calculated. The results are shown in Table V. From Table V it is seen that, only when site I is assigned to molecule 1, site II to molecule 3, site III to molecule 2, and site IV to molecule 4, is the g_{zz} direction close to the Cu–O(2) bond (C_2 axis of the molecule) with a similar minimum angle of 12° and is g_{xx} direction very close to the Cu–N(4) or Cu–N(1) bond (pseudo C_3 axis) with a similar minimum angle of 6° for the four-site **g** tensor with respect to four magnetically inequivalent Cu sites. The assignment of **g** tensors to the other four molecules related by a center of inversion is performed by symmetry operation. The obtained assignment indicates that the principal axis of g_{zz} is close to the Cu–O(2) bond with a similar minimum angle of 12°, g_{xx} is close to the Cu–N(4) and Cu–N(1) bonds with a similar minimum angle of 6°, and the axis of g_{yy} is close to the Cu–N(2) or Cu–N(3) bond with a similar angle of 19°. The directions of the principal axes of the **g** and **A** tensors of four sites with respect to the experimental frame (x, y, z, i.e., a, b, c) and those of the **g** tensors with respect to the structure of the Zn(2) site fragment of the molecule are shown in Figure 4. The principal axes of g_{zz} for four sites in the unit cell are marked by arrows in Figure 5.

The principal values listed in Table IV are quite near to those of Cu,Zn–BeSOD (where the principal values of the **g** tensor are

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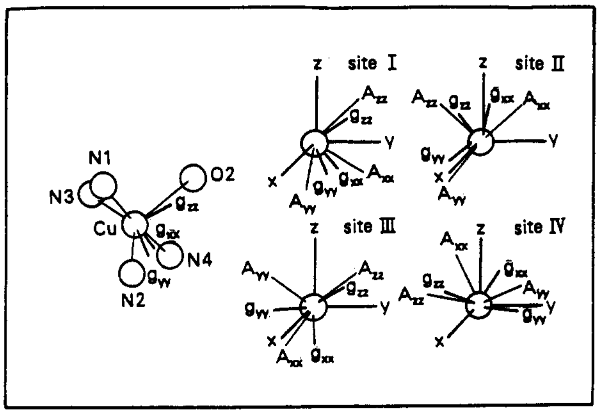

Figure 4. Directions of the principal axes of the **g** and **A** tensors for four sites with respect to the experimental frame (x, y, z, i.e., a, b, c) and those of the **g** tensor with respect to the structure of the CuN_4O fragment corresponding to the Zn(2) site in mixed crystal.

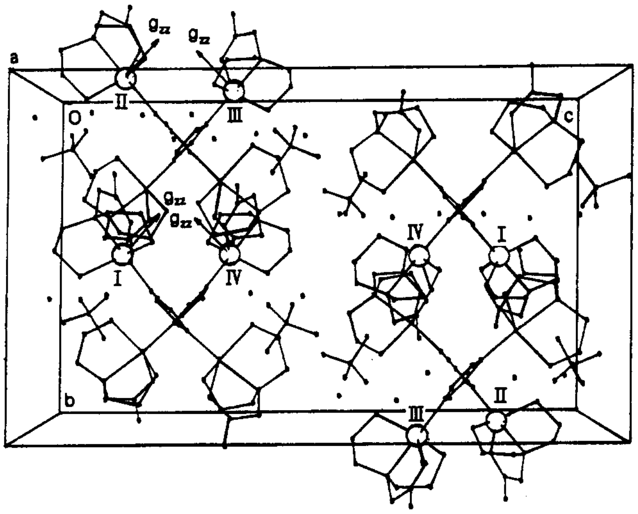

Figure 5. Directions of g_{zz} for four Cu^{2+} sites with respect to the molecules in the unit cell.

2.03, 2.09, and 2.26; those of the **A** tensor are 34.6×10^{-4}, 52.2×10^{-4}, and 142×10^{-4} cm^{-1}).[2]

For square pyramidal complexes, the unpaired electron is in the $d_{x^2-y^2}$ orbital, so that the **g** and **A** value patterns are similar to those observed for square planar[15,18] and can be approximately expressed by[19,20]

$$g_\parallel = g_e - 8\rho(\alpha\beta_1 - U) \qquad (3a)$$

$$g_\perp = g_e - 2\mu(\alpha\beta - Z) \qquad (3b)$$

$$A_\parallel = P\left[-\alpha^2\left(\frac{4}{7} + \kappa_0\right) + (g_\parallel - g_e) + \frac{3}{7}(g_\perp - g_e) - 8\rho U - \frac{6}{7}\mu Z\right] \qquad (3c)$$

$$A_\perp = P\left[\alpha_2\left(\frac{2}{7} - \kappa_0\right) + \frac{11}{14}(g_\perp - g_e) - \frac{22}{14}\mu Z\right] \qquad (3d)$$

where

$$U = \alpha'\beta_1 S + \alpha'(1 - \beta_1^2)^{1/2}[T(n)]/2$$

$$Z = \alpha'\beta S + \alpha'(1 - \beta^2)^{1/2}[T(n)]/\sqrt{2}$$

$$\rho = \frac{\lambda\alpha\beta_1}{\Delta E_{xy}}$$

$$\mu = \frac{\lambda\alpha\beta}{\Delta E_{xz,yz}}$$

and where $P = 2\gamma\beta_0\beta_N\langle r^{-3}\rangle = 0.0036$ cm^{-1}, $T(n) = 0.2765$, $\lambda = -828$ cm^{-1} is the spin–orbit coupling constant for the free Cu(II) ion, $g_e = 2.0023$ is the electron value, κ_0 is the Fermi constant term for the free Cu(II) ion, and the constants α, α', β, and β_1 are the mixing parameters for the molecular orbitals. Transition energies $\Delta E = E_{xy} - E_{x^2-y^2} = 14\,300$ cm^{-1} were approximately obtained from powder reflectance spectroscopy and $\Delta E_{xz,yz} = 17\,500$ cm^{-1} was estimated,[21] because a 20% error on ΔE_{xy} and $\Delta E_{xz,yz}$ results in only about a 5% error in β and β_1, respectively.[19]

Following the iterative method and using our experimental values for $g_\parallel = g_{zz}$, $g_\perp = (g_{xx} + g_{yy})/2$, $A_\parallel = A_{zz}$, and $A_\perp = (A_{xx} + A_{yy})/2$, we obtain the following parameters:

$$\alpha = 0.76 \qquad \beta_1^2 = 0.68 \qquad \beta^2 = 0.93 \qquad \kappa_0 = 0.39$$

The values obtained for α^2 and β_1^2 indicate a covalent character for the in-plane σ and π bonding, respectively, while β^2 indicates ionic out-of-plane π bonding.

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Supplementary Material Available: Tables giving atomic coordinates and isotropic thermal parameters, complete bond lengths and bond angles, complete atom positional parameters, anisotropic thermal parameters, and torsional angles and diagrams showing molecular and unit cell structures (29 pages). Ordering information is given on any current masthead page.

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