Inorg. Chem. **1995,** *34,* 2889−2893

Synthesis, Crystal Structure, and Properties of a New Imidazolate-Bridged Copper−Zinc Heterobinuclear Complex with Triethylenetetramine Ligands

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Received June 3, 1994[®]

The syntheses of the mononuclear [(trien)Cu(imH)]$(ClO_4)_2$ and binuclear [(trien)Cu(im)Cu(trien)]$(ClO_4)_3{\cdot}H_2O$ and [(trien)Cu(im)Zn(trien)]$(ClO_4)_3{\cdot}H_2O$ complexes, where trien = triethylenetetramine and im is the imidazolate ion, are described. Single-crystal X-ray diffraction studies of the heterobinuclear complex reveals the geometry of the imidazolate-bridged Cu(II)−Zn(II) center. The copper or zinc atom is pentacoordinate, with four trien nitrogen atoms forming an approximate plane and a bridging imidazolate in the apical position of a distorted tetragonal pyramid. The Cu−Zn distance is 6.081(2) Å. pH-dependent ESR studies of frozen 50% aqueous DMSO solutions of [Cu(trien)]$(ClO_4)_2$, [Cu(trien)(imH)]$(ClO_4)_2$, and [(trien)Cu(im)Zn(trien)]$(ClO_4)_3{\cdot}H_2O$ complexes have also been carried out and show that the bridged cation $[(trien)Cu(im)Zn(trien)]^{3+}$ exists as a major species in solution over the range $10.3 \le pH \le 12.4$. As the pH is lowered to 9.6−10.3, the bridge is broken on the copper side, which is different from case of [(dtma)Cu(im)Zn(dtma)]ClO_4 and [(tren)Cu(im)Zn(tren)]$[ClO_4]_3$, where the bridge is broken on the zinc side.

Introduction

Syntheses and characterizations of discrete imidazolate-bridged copper(II)−zinc(II) heterobinuclear complexes have been of interest since an imidazolate-bridged copper(II)−zinc(II) center was discovered in bovine erythrocyte superoxide diamutase (Cu/Zn-SOD).[1,2] However, attempts to synthesize these complexes with various ligands, such as 2-(4-imidazolyl)-1,5,9-triazacyclododecane and tris((*N*-methylbenzimidazol-2-yl)methyl)amine, have failed and some homobi- and polynuclear complexes bridged by an imidazolate anion have been reported.[3−6] Until recently, only two such compounds, [(tren)Cu(im)Zn(tren)]$(ClO_4)_3$ (tren = tris(2-aminoethyl)amine) and [(dtma)Cu(im)Zn(dtma)]ClO_4 (dtma = diethylenetriamine-*N*′-acetate),[7,8] were prepared with tripodal ligands and structurally elucidated by X-ray diffraction. In order to better elucidate the chemical nature of the imidazolate-bridged Cu−Zn center of SOD in a simple model system, in particular, the breaking behavior of the imidazolate bridge at low pH and its origin, we report here the synthesis, crystal structure, and properties of [(trien)Cu(im)Zn(trien)]$(ClO_4)_3{\cdot}H_2O$, which is the first Cu−im−Zn complex prepared from chain polyamine ligand (trien = triethylenetetramine) and is also the first example of the imidazolate bridge breaking on the copper side at low pH rather than the zinc side. In this complex, the bridging imidazolate occupies the apical position of a distorted tetragonal pyramid compared with the basal plane position in [(dtma)Cu(im)Zn(dtma)]ClO_4 as reported. We also report syntheses and properties of [(trien)Cu(imH)]$(ClO_4)_2$ and [(trien)Cu(im)Cu(trien)]$(ClO_4)_3{\cdot}H_2O$.

Experimental Section

Preparation. All reagents were reagent grade. The compounds [Cu(trien)]$(ClO_4)_2$ (**1**) and [Zn(trien)]$(ClO_4)_2$ (**2**) were prepared as described previously in the literature.[9] Other complexes were prepared as follows.

[Cu(trien)imH]$(ClO_4)_2$ (3). To a solution containing 0.408 g (1.0 mmol) of **1** in the 15 mL of water was added 0.068 g (1.0 mmol) of imidazole. After being stirred for 0.5 h, the solution was filtered and the filtrate was concentrated at about 70 °C until a blue crystalline product precipitated. Yield: 72%. Anal. Calcd for $C_9H_{22}N_6Cl_2O_8Cu$ (**3**): C, 22.67; H, 4.65; N, 17.63; Cu, 13.33. Found: C, 22.24; H, 4.51; N, 18.06; Cu, 13.12.

[(trien)Cu(im)Zn(trien)]$(ClO_4)_3{\cdot}H_2O$ (4). A 0.477 g (1.0 mmol) sample of **3** and 0.410 g (1.0 mmol) of **2** were mixed in 15 mL of water, and then 1.0 mL (1.0 mol/L) of NaOH solution was added with stirring. After filtration, the filtrate was allowed to evaporate slowly under vacuum, and a few days later, blue crystals were obtained. Yield: ca. 50%. Anal. Calcd for $C_{15}H_{41}N_{10}Cl_3O_{13}CuZn$ (**4**): C, 22.39; H, 5.13; N, 17.40; Cu, 7.89; Zn, 8.12. Found: C, 22.70; H, 5.47; N, 17.76; Cu, 7.73; Zn, 8.44.

[(trien)Cu(im)Cu(trien)]$(ClO_4)_3{\cdot}H_2O$ (5). Complex **5** was prepared similarly to **4** except that **1** was used instead of **2**. Yield: ca. 42%. Anal. Calcd for $C_{15}H_{41}N_{10}Cl_3O_{13}Cu_2$ (**5**): C, 22.44; H, 5.15; N, 17.44; Cu, 15.82. Found: C, 22.66; H, 5.14; N, 17.72; Cu, 15.65.

Caution! *Perchlorate salts of compounds containing organic ligands are potentially explosive!*[10]

Physical Measurements. Electronic spectra were performed in the range 200−1500 nm with a UV-3100 UV/vis/near-IR recording spectrophotometer. The polycrystalline powder ESR spectra of **4** and **5** at room temperature and the 110 K ESR spectra of **1**, **3**, and **4** in frozen absolute dimethyl sulfoxide (DMSO) solutions and frozen 50% aqueous DMSO solutions as a function of pH were recorded with a Bruker ER200D-SRC spectrometer employing X-band radiation and a cylindrical cavity with 100-kHz magnetic field modulation. Calibrations

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Table 1. Crystal Data for Complex **4**

formula	$C_{15}H_{41}N_{10}Cl_3O_{13}CuZn$
fw	804.82
space group	$P\bar{1}$
a (Å)	13.262(2)
b (Å)	13.695(4)
c (Å)	8.88(2)
α (deg)	97.64(2)
β (deg)	91.95(2)
γ (deg)	88.69(2)
V (Å^3)	1597.5
Z	2
d_c (g cm^{-3})	1.67
μ(Mo Kα) (cm^{-1})	17.6
crystal size	0.08 × 0.18 × 0.38
λ(Mo Kα) (Å)	0.709 30
no. of orientation reflns	25
range of orientation reflns (deg)	$10 < 2\theta < 14$
data collection range (deg)	$2 < 2\theta < 50$
no. of unique data	5496
total with $F_o^2 > 3.0\sigma(F_o^2)$	3162
R^a	0.073
R_w^b	0.081
max peak in final diff map (e/Å^3)	0.77(12)

[a] $R = \sum|F_o - F_c|/\sum F_o$. [b] $R_w = (\sum w(F_o - F_c)^2/\sum wF_o^2)^{1:2}$; $w = 1$.

of the microwave frequency were performed with an EIP845A microwave frequency counter.

X-ray Diffraction Studies. Cell parameters and reflection intensities were measured at 292(2) K on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. The Enraf Structure Determination Package[11] was used for data collection, processing, and structure solution. Intensity data were corrected for anisotropic decay, empirical absorption, and LP effects. The structure was solved by direct methods.[12] An initial E map and successive difference Fourier maps revealed the coordinates of all the atoms. The C21 atom in one trien ligand and O9 and O10 atoms in one of the ClO_4^- groups were found to exhibit local positional disorder. The hydrogen atoms were included in the refinement but restrained to ride on the atoms to which they are bonded. The structure was refined by full-matrix least-squares procedures where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as 1.0 for all observed reflections. Thermal parameters for oxygen atoms of the ClO_4^- groups and some carbon and nitrogen atoms of the trien ligands were substantially larger than those of the remaining atoms. Scattering factors were taken from Cromer and Waber.[13] Crystal data, atomic parameters and temperature factors, and selected bond distances and angles are given in Tables 1−3, respectively. Additional crystal and refinement data and complete lists of coordinates, anisotropic thermal parameters, bond distances and angles are available in the supplementary material.

Table 2. Atomic Positional and Thermal Parameters for **4**

atoms	x	y	z	B (Å^2)	mult
Cu	0.7526(1)	0.43841(9)	0.3736(2)	4.28(3)	1.000
Zn	0.7558(6)	0.84528(9)	0.7438(2)	4.40(3)	1.000
N1	0.7589(8)	0.6997(6)	0.677(1)	4.5(2)	1.000
C2	0.7529(9)	0.6488(8)	0.539(1)	4.5(3)	1.000
N3	0.7550(8)	0.5541(6)	0.544(1)	4.4(2)	1.000
C4	0.762(1)	0.5408(8)	0.689(1)	6.6(4)	1.000
C5	0.765(1)	0.6322(8)	0.773(1)	7.2(4)	1.000
N6	0.8693(9)	0.3438(8)	0.434(1)	7.1(3)	1.000
C7	0.960(1)	0.369(1)	0.362(2)	8.8(5)	1.000
C8	0.936(1)	0.392(1)	0.206(2)	8.0(4)	1.000
N9	0.8551(9)	0.4650(9)	0.210(1)	6.6(3)	1.000
C10	0.801(1)	0.464(2)	0.069(2)	13.9(8)	1.000
C11	0.702(1)	0.475(2)	0.065(2)	12.6(7)	1.000
N12	0.6488(8)	0.4721(8)	0.203(1)	6.5(3)	1.000
C13	0.568(1)	0.399(1)	0.185(2)	7.9(4)	1.000
C14	0.544(1)	0.380(1)	0.342(2)	8.2(5)	1.000
N15	0.6369(9)	0.3477(7)	0.423(1)	6.9(3)	1.000
N16	0.663(1)	0.8559(9)	0.935(1)	10.6(4)	1.000
C17	0.568(1)	0.883(1)	0.874(3)	13.0(7)	1.000
C18	0.562(1)	0.951(1)	0.773(3)	12.6(7)	1.000
N19	0.633(1)	0.9128(9)	0.648(2)	8.8(4)	1.000
C20	0.663(2)	0.985(1)	0.560(2)	14.1(7)	1.000
C21	0.751(3)	0.957(2)	0.481(3)	13(1)	0.627
C21′	0.773(5)	1.008(3)	0.589(4)	15(2)	0.373
N22	0.830(1)	0.917(1)	0.585(2)	10.7(4)	1.000
C23	0.912(2)	0.972(1)	0.666(3)	24.3(8)	1.000
C24	0.924(2)	0.939(2)	0.786(4)	26(1)	1.000
N25	0.890(2)	0.886(1)	0.883(2)	16.5(6)	1.000
Cl1	0.9572(3)	0.7372(3)	0.2241(5)	7.8(1)	1.000
Cl2	0.5175(3)	0.7298(3)	0.2534(5)	7.5(1)	1.000
Cl3	0.7559(3)	1.1180(2)	1.1401(5)	6.95(9)	1.000
O1	1.016(1)	0.779(1)	0.126(2)	15.8(6)[a]	1.000
O2	0.999(1)	0.644(1)	0.245(2)	14.1(5)[a]	1.000
O3	0.966(1)	0.791(1)	0.361(2)	16.7(6)[a]	1.000
O4	0.860(2)	0.735(2)	0.172(2)	19.5(7)[a]	1.000
O5	0.525(1)	0.779(1)	0.395(2)	16.3(6)[a]	1.000
O6	0.446(1)	0.774(1)	0.164(2)	12.5(4)[a]	1.000
O7	0.481(1)	0.635(1)	0.274(2)	11.7(4)[a]	1.000
O8	0.607(1)	0.720(1)	0.186(2)	15.7(6)[a]	1.000
O9	0.671(2)	1.144(2)	1.227(3)	14.4(8)[a]	0.631
O9′	0.710(4)	1.207(4)	1.114(3)	16(2)[a]	0.369
O10	0.796(2)	1.020(2)	1.153(3)	9.2(6)[a]	0.509
O10′	0.703(2)	1.032(2)	1.151(3)	12.3(8)[a]	0.491
O11	0.757(2)	1.124(2)	0.995(3)	25(1)[a]	1.000
O12	0.829(2)	1.148(2)	1.234(3)	23.4(9)[a]	1.000
O13	0.761(1)	0.268(1)	−0.281(2)	12.0(4)[a]	1.000

[a] $B = {}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4**

Cu−N3	2.042(6)	Cu−N6	2.098(7)
Cu−N9	2.092(7)	Cu−N12	2.104(7)
Cu−N15	2.090(7)	Zn−N1	2.003(5)
Zn−N16	2.116(9)	Zn−N19	2.068(9)
Zn−N22	2.110(10)	Zn−N25	2.170(20)
N1−C2	1.331(8)	N1−C5	1.338(9)
C2−N3	1.305(8)	N3−C4	1.326(9)
C4−C5	1.370(9)		
N3−Cu−N6	104.5(3)	N3−Cu−N9	108.6(3)
N3−Cu−N12	108.6(3)	N3−Cu−N15	105.9(3)
N6−Cu−N9	82.0(3)	N6−Cu−N12	146.3(3)
N6−Cu−N15	94.7(3)	N9−Cu−N12	81.3(3)
N9−Cu−N15	145.0(3)	N12−Cu−N15	82.7(3)
N1−Zn−N16	101.6(3)	N1−Zn−N19	111.5(3)
N1−Zn−N22	109.4(4)	N1−Zn−N25	109.4(4)
N16−Zn−N19	83.1(5)	N16−Zn−N22	148.5(4)
N16−Zn−N25	92.7(6)	N19−Zn−N22	80.5(5)
N19−Zn−N25	138.9(5)	N22−Zn−N25	82.6(7)
Cu−N3−C2	130.5(6)	Zn−N1−C2	130.6(6)

Results and Discussion

Description of Structure. The molecular structure of **4** is shown in Figure 1. The complex consists of a [(trien)Cu(im)-Zn(trien)]$^{3+}$ cation, three ClO_4^- anions, and one water molecule. In the cation, the Cu and Zn atoms are bridged by the imidazolate anion, forming a heterobinuclear complex. The coordination polyhedron around each of the metal ions is better described as a distorted tetragonal pyramid (TP), in which the nitrogen atom of the im group occupies the distorted axial position and four nitrogen atoms of the trien situate on the approximate basal plane; *i.e.*, the two near TP polyhedrons are bridged by the imidazolate ion through their apical positions. This bridged form is different from that in [(dtma)Cu(im)Zn-

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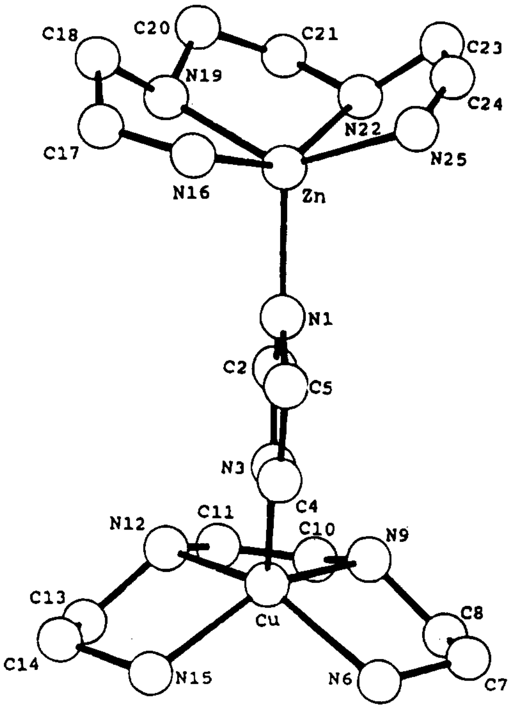

Figure 1. Molecular structure of $[(\mathrm{trien})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{trien})]^{3+}$.

$(\mathrm{dtma})]\mathrm{ClO_4}$, in which two distorted TP polyhedrons are bridged by the imidazolate ion through their approximate plane positions, and from that in $[(\mathrm{tren})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{tren})](\mathrm{ClO_4})_3$, in which two distorted TBP polyhedrons are bridged by the imidazolate ion through their distorted axial positions. The best planes are calculated through N6, N9, N12, and N15 around the Cu atom and N16, N19, N22, and N25 around the Zn atom, the separations of the Cu and Zn atoms from which are 0.605(1) and 0.648 Å, respectively. The distortion (Δ) of the coordination polyhedron from a regular tetragonal pyramid ($\Delta = 1$) toward a regular trigonal bipyramid ($\Delta = 0$) has been calculated according to the literature reported by Mutterties and Galy.[14,15] $\Delta = 0.93$ for Cu and $\Delta = 0.79$ for Zn indicate that the geometries of coordination around both metal atoms are very close to TP in different degrees, closer to TP than that in $[(\mathrm{dtma})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{dtma})]\mathrm{ClO_4}$ as reported.

In complex **4**, the average bond length of $\mathrm{Cu{-}N_{plane}}$ (2.096 Å) is slightly shorter than that of $\mathrm{Zn{-}N_{plane}}$ (2.116 Å), which is consistent with corresponding values reported for $[(\mathrm{dtma})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{dtma})]\mathrm{ClO_4}$.[7] Although the bond length of $\mathrm{Zn{-}N_{im}}$ along with axial orientation of the TP (Zn–N1 = 2.003(5) Å) is in agreement with corresponding values (1.992(4) and 1.970(4) Å) for $[(\mathrm{trien}(\mathrm{Zn}(\mathrm{im})\mathrm{Zn}(\mathrm{trien})](\mathrm{ClO_4})_3$,[16] the bond length of $\mathrm{Cu{-}N_{im}}$ (Cu–N3 = 2.042(6) Å) is obviously longer than those in the above-mentioned complexes but is consistent with the larger length normally observed in the axial direction of the TP.[17,18] The distance between the Cu and Zn atoms in $[(\mathrm{trien})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{trien})](\mathrm{ClO_4})_3$ is 6.081(2) Å, which is shorter than that in Cu/Zn-SOD (Cu···Zn = 6.3 Å) and those in $[(\mathrm{dtma})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{dtma})]\mathrm{ClO_4}$ and $[(\mathrm{tren})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{tren})](\mathrm{ClO_4})_3$ as reported. In view of the little difference between average Cu–N and Zn–N bond lengths and the same coordination geometries around the metals with similar distortions, the possibility of interchanging the Cu and Zn atoms in the same molecule cannot be eliminated. In addition, there are a lot of intramolecular and intermolecular hydrogen bonds in the unit cell (see supplementary material).

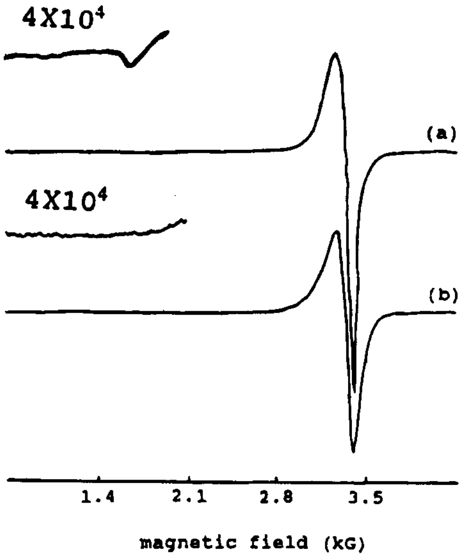

Figure 2. Polycrystalline powder ESR spectra at room temperature: (a) complex **5**; (b) complex **4**.

Electronic Spectra. The electronic spectra of complexes **4** and **5** were recorded, and the maxima at 15 100 and 15 500 $\mathrm{cm^{-1}}$, respectively, are assigned to d–d transitions. These data suggest a tetragonal pyramidal coordination geometry for the copper atoms. The energies of the d–d transitions in tetragonal pyramidal $\mathrm{CuN_5}$ chromophores usually lie in the range 13 000–17 000 $\mathrm{cm^{-1}}$.[19] In $[(\mathrm{trien})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{trien})](\mathrm{ClO_4})_3$, a slight red shift of the electronic transitions may arise from the influence of the imidazolate bridging the heteronuclear atoms. This indicates that complex **4** is a mixed Cu/Zn complex and not a mixture of Cu/Cu and Zn/Zn complexes.

ESR Spectra. The X-band ESR spectra of both binuclear complexes were measured in polycrystalline powder at room temperature and are shown in Figure 2. Signals of $\Delta M = \pm 1$ as a single broad absorption appear at $g = 2.077$ for **4** and $g = 2.064$ for **5**, respectively. The absence of hyperfine structure indicates that the interaction would be mainly dipolar in character. In addition, a $\Delta M = \pm 2$ half-field signal is observed at $g \sim 4.138$ for **5** at room temperature, and the same is indicated at low temperature (110 K). This suggests a weak magnetic interaction between two Cu ions through an imidazolate bridge. However, the absence of a $\Delta M = \pm 2$ signal for **4** at room temperature and 110 K means that the presence of Cu–im–Cu impurities in **4** can be eliminated; *i.e.*, complex **4** consists only of a heterobinuclear Cu/Zn complex. In order to obtain more detailed electronic structure information about the Cu(II) ion in **4**, the powder ESR spectrum of **4** diluted in a Zn–im–Zn complex was measured, and the hyperfine structure was observed ($g_{\parallel} = 2.217$ and $A_{\parallel} = 165$ G). These parameters indicate that the local symmetry of the Cu(II) ion is nearly square pyramidal with mainly a $d_{x^2-y^2}$ ground state.[20]

The 110 K ESR spectra of **1**, **3**, and **4** in absolute DMSO solution, which are characterized by nearly axial symmetry, are shown in Figure 3, and the corresponding spectral parameters are listed in Table 4. The ESR data, especially $A_{\parallel}$, show

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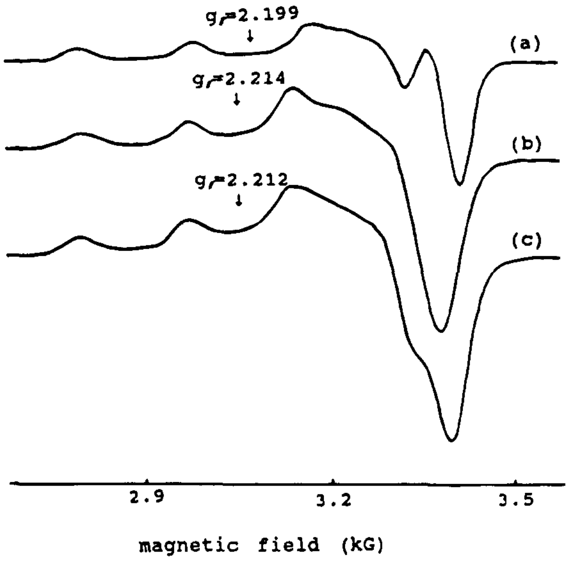

Figure 3. ESR spectra of frozen absolute dimethyl sulfoxide solutions at 110 K: (a) complex **1**; (b) complex **3**; (c) complex **4**.

Table 4. ESR Spectral Parameters

complex **1**			complex **3**			complex **4**		
pH	$g_\parallel$	$A_\parallel$ (G)	pH	$g_\parallel$	$A_\parallel$ (G)	pH	$g_\parallel$	$A_\parallel$ (G)
			(a) Absolute DMSO					
	2.199	188		2.214	169		2.212	174
			(b) 1:1 H_2O–DMSO					
2.7	2.410	116	2.8	2.410	116	2.7	2.410	116
	2.237	182		2.237	182		2.237	182
3.6	2.237	182	3.6	2.237	182	3.1	2.237	182
	2.199	188		2.201	188		2.200	188
5.1	2.199	188	5.0	2.201	188	3.6	2.200	188
7.7	2.199	188	6.4	2.201	187	5.2	2.201	189
11.5	2.200	189	8.7	2.215	169	7.4	2.200	188
			11.8	2.215	169	8.7	2.200	188
						9.6	2.200	188
						10.3	2.213	174
						11.4	2.213	174
						12.4	2.213	174

appreciable differences so the breakdown of the imidazolate bridge on one of the metal ions of complex **4** in the solution at low pH would be determined by comparing ESR spectral parameters obtained at different pH.[21]

The 110 K ESR spectra of complex **1** in frozen 50% aqueous DMSO solution as a function of pH was measured, and the spectral parameters are summarized in Table 4. The ESR spectra reflect the presence of at least three different axially or nearly axially symmetric species in solutions under different pH conditions. Such possibilities exist for **1**, **6**, and **7**. At high pH, **1** is clearly present in solution with the appearance of $g_\parallel$ at 2.199 with $A_\parallel$ = 188 G, which are in agreement with those of complex **1** in absolute DMSO. As the pH is lowered to 3.6, the presence of monodentate, bidentate, or tridentate trien complexes is shown by the ESR signal having $g_\parallel$ = 2.237 and $A_\parallel$ = 182 G. At low pH, it is likely that the trien ligand is dissociated according to

$$\underset{\mathbf{1}}{[\mathrm{Cu(trien)}]^{2+}} \underset{\mathrm{pH\ 3.6}}{\overset{\mathrm{H^+}}{\rightleftharpoons}} \underset{\mathbf{6}}{[\mathrm{Cu(H}_n\mathrm{trien)(H_2O)}_n]^{(2+n)+}} \underset{\mathrm{pH\ 2.7}}{\overset{\mathrm{H^+}}{\rightleftharpoons}} \underset{\mathbf{7}}{[\mathrm{Cu(H_2O)_6}]^{2+}} \quad (1)$$

The presence of **7** was verified by observing $g_\parallel$ at 2.411 with $A_\parallel$ = 118 G, which is quite near those of $[Cu(H_2O)_6]^{2+}$ in the same frozen solutions.[22]

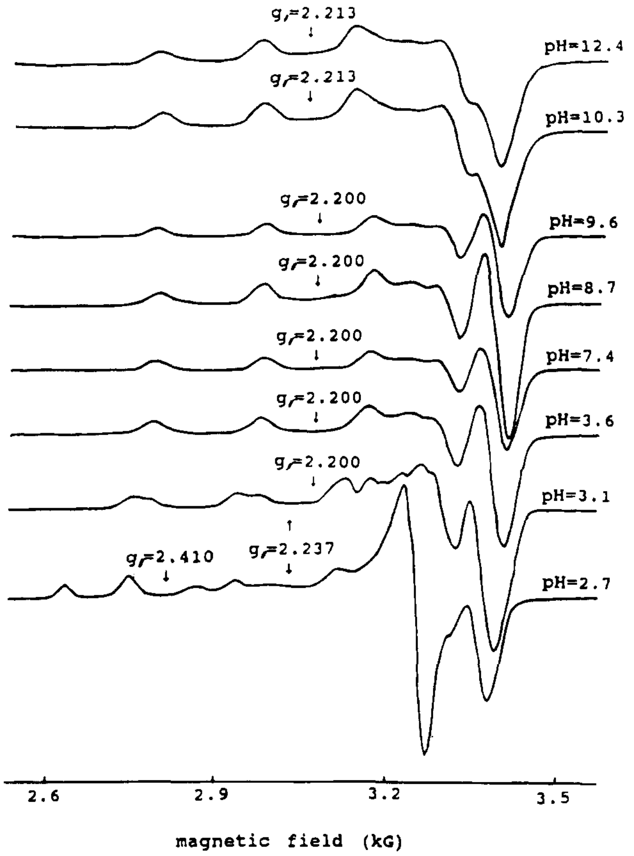

Figure 4. ESR spectra of frozen 50% aqueous DMSO solutions of complex **4** at 110 K. pH: 12.4; 10.3; 9.6; 8.7; 7.4; 3.6; 3.1; 2.7.

Frozen solutions of complex **3** also display nearly axial ESR spectra at 110 K, indicative of mixtures. The $g_\parallel$ and $A_\parallel$ values are collected in Table 4. Although **3** is a major component of the mixture at weak alkaline pH, **1** forms at low pH and **8** is probably present at pH ~11.8 due to the pK_a (10.0) of imH. It is not possible from the ESR spectra to distinguish complexes **3** and **8**. At lower pH the trien ligand is also dissociated according to eq 1. The ESR spectra are consistent with eqs 2 and 3 for low- and high-pH solutions, respectively. The pH

$$\underset{\mathbf{3}}{[\mathrm{Cu(trien)(imH)}]^{2+}} \underset{6.4\ <\ \mathrm{pH}\ <\ 8.7}{\overset{\mathrm{H^+}}{\rightleftharpoons}} \underset{\mathbf{1}}{[\mathrm{Cu(trien)}]^{2+}} + \mathrm{imH_2}^+ \quad (2)$$

$$\underset{\mathbf{3}}{[\mathrm{Cu(trien)(imH)}]^{2+}} \underset{\mathrm{pH}\ \sim 11.4}{\overset{\mathrm{OH^-}}{\rightleftharpoons}} \underset{\mathbf{8}}{[\mathrm{Cu(trien)(im)}]^{+}} \quad (3)$$

for the dissociation of imH in **3** is higher than that reported for $[Cu(dtma)(imH)]ClO_4$, the latter having pH ~5.0. This result indicates that the dissociation of imH from $[Cu(trien)(imH)]^{2+}$ is easier than that of imH from $[Cu(dtma)(imH)]^+$; *i.e.*, in the TP, the coordination of imH to Cu(II) is weaker along the axial direction than it is in the plane.

Figure 4 shows the pH-dependent ESR spectra of frozen solutions of **4** at 110 K. Spectral parameters are included in Table 4. Decreasing the pH will break the imidazolate bridge. When the pH is between 10.3 and 12.4, the $g_\parallel$ of 2.213 and $A_\parallel$ of 175 G, which are in agreement with those of complex **4** in

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[21] O'young, C.-L.; Dewan, J. C.; Lilienthal, H. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 7291.

[22] O'Young, C.-L.; Lippard, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 4920.

absolute DMSO, indicate that the major component in the solution is heterobinuclear **4**. In the pH range 3.6−9.6, the $g_{\parallel}$ value of 2.200 and $A_{\parallel}$ value of 188 G are quite near the corresponding values of mononuclear **1** in absolute DMSO solution. All these results show that the imidazolate bridge is broken on the Cu(II) side in the pH range 9.6−10.3 according to one of the following:

$$\underset{\mathbf{4}}{[(\mathrm{trien})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{trien})]^{3+}} \xrightleftharpoons[9.6\ <\ \mathrm{pH}\ <\ 10.3]{\mathrm{H}^+} \underset{\mathbf{1}}{[\mathrm{Cu}(\mathrm{trien})]^{2+}} + [\mathrm{Zn}(\mathrm{trien})(\mathrm{imH})]^{2+} \quad (4)$$

$$\underset{\mathbf{4}}{[(\mathrm{trien})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{trien})]^{3+}} \xrightleftharpoons[9.6\ <\ \mathrm{pH}\ <\ 10.3]{\mathrm{H}^+} \underset{\mathbf{1}}{[\mathrm{Cu}(\mathrm{trien})]^{2+}} + \mathrm{imH} + [\mathrm{Zn}(\mathrm{trien})]^{2+} \quad (5)$$

Since $[\mathrm{Cu}(\mathrm{trien})(\mathrm{imH})]^{2+}$ can stably exist in the solution of **3** at pH ≥8.6, protonated imH in the solution of **4** would coordinate with the Cu(II) unless it coordinates with the Zn(II) at the corresponding pH value. However, the ESR signal of $[\mathrm{Cu}(\mathrm{trien})(\mathrm{imH})]^{2+}$ is not found for the solution at the same pH, so imH probably remains to coordinate to Zn(II) at pH 8.6−9.6 after the breakdown of the imidazolate bridge. The major species in the solution are $[\mathrm{Cu}(\mathrm{trien})]^{2+}$ and $[\mathrm{Zn}(\mathrm{trien})(\mathrm{imH})]^{2+}$; *i.e.*, the imidazolate bridge still remains to coordinate with Zn(II) when it is broken on the Cu(II) side in the range pH 9.6−10.3 according to eq 4. In a similar manner, with decreasing pH, free cupric ion and $\mathrm{H_4trien}^{4+}$ are ultimately produced according to eq 1.

The above-mentioned result, that the imidazolate bridge in complex **4** is first broken on the Cu(II) side in the pH range 9.6−10.3, is different from that previously reported, *i.e.* that the imidazolate bridge in $[(\mathrm{dtma})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{dtma})]\mathrm{ClO_4}$ is first broken on the Zn(II) side in the same pH range.[8] The mode of dissociation may be regarded as a discrepancy of their molecular structures. In $[(\mathrm{dtma})\mathrm{Cu}(\mathrm{im})\mathrm{Zn}(\mathrm{dtma})]\mathrm{ClO_4}$, the geometry of coordination around the two metal ions is distorted TP and the imH occupies a position on the approximate basal plane. When the imidazolate bridge is broken on the Zn(II) side, the geometry around the Cu(II) ion still remains stable distorted TP and the geometry around the Zn(II) ion transforms to stable tetrahedral, which is relatively unstable for the Cu(II) ion. In complex **4**, the geometry around two metal ions is nearly TP and the imH occupies the axial position. When the imidazolate bridge is broken on the Cu(II) side, the geometry around the Zn(II) ion still remains stable approximately TP and the geometry around the Cu(II) ion transforms to stable tetragonal, which is relatively unstable for the Zn(II) ion.

Supplementary Material Available: Listings of crystallographic data, hydrogen positional parameters, thermal parameters, bond lengths and angles, hydrogen-bonding parameters, and least-squares planes and a packing diagram of the unit cell (16 pages). Ordering information is given on any current masthead page.

IC940638+