Crystal Structure of [Chloro[tris[(1-ethyl-1*H*-benzimidazol-2-yl)-methyl]amine]zinc(II)] Tetraphenylborate Acetone

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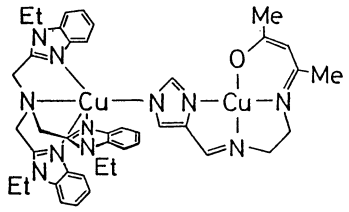
Synopsis. The crystal structure of the title complex has been determined by the single-crystal X-ray diffraction method. The zinc complex has approximately a trigonal bipyramidal coordination geometry, which is different from the copper(II) complex with the same tripod ligand.

The X-ray crystal structure of bovine erythrocyte superoxide dismutase(BESOD) has elucidated the specific binuclear structure of the active site, in which a zinc ion with a tetrahedral coordination sphere is linked to a cooper(II) ion with a square planar geometry through an imidazolate group.[1] In order to obtain the physical properties, the zinc ion has been substituted by copper(II) or cobalt(II) ion and the magnetic parameters have been obtained.[2,3] It is questionable whether the metal replaced compound has the same structure as the original complex. In a series of our studies on imidazolate-bridged binuclear complexes, we have shown an effective synthetic method which can mimic the structural characteristics of the active site of BESOD.[4-6] By applying the synthetic method, an imidazolate-bridged binuclear copper(II)-copper-(II) complex, **1**, has been prepared and its crystal structure has been determined.[4] In this study, we report on the crystal structure of the title zinc complex with the same tripod ligand, **2**.



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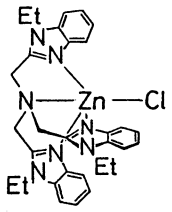

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Experimental

Synthesis. The tripod ligand tris[(1-ethyl-1*H*-benzimidazol-2-yl)methyl]amine (abbreviated as NTBEt) was prepared by a method described in the literature.[7]

[Zn(Cl⁻)(NTBEt)][BPh₄]·Acetone. To a solution of NTBEt (2 mmol) in 20 cm³ of acetone was added a solution of zinc(II) chloride (2 mmol) in 10 cm³ of methanol. The solution was warmed in a water bath for 10 min and then filtered. To the filtrate was added a solution of sodium tetraphenylborate (2 mmol) in 10 cm³ of methanol. After several hours, colorless prisms precipitated and were collected by suction filtration. Found: C, 70.34; H, 6.11; N, 10.04%. Calcd for $ZnClC_{54}H_{53}N_7B\cdot(CH_3)_2C{=}O$: C, 70.60; H, 6.13; N, 10.11%. Λ_M 144 S mol^{-1} cm^2 (in acetonitrile).

Physical Measurements. The elemental analysis was performed by Mr. Shinichi Miyazaki at The Technical Service Center of Kumamoto University. The molar electrical conductance was measured on a Denki Kagaku Keiki AOC-10 digital conductometer in 10^{-3} mol dm^{-3} solutions. The magnetic susceptibility was measured by the Faraday method at room temperature.

X-Ray Diffraction Study. Diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer at the Faculty of Science, Kyushu University, using graphite monochromatized Mo$K\alpha$ radiation at 20 °C. Information concerning conditions for crystallographic data collection and structure refinement is summarized below. [Zn(Cl⁻)(NTBEt)][BPh₄]·Acetone, Formula=$ZnClON_7C_{57}BH_{59}$ F.W.=969.7, triclinic, space group $P\bar{1}$, a=14.009(2) Å, b=17.372(2) Å, c=11.607(1) Å, α=95.52(1)°, β=113.08(1)°, γ=76.75(1)°, V=2529.4 Å^3, D_{calcd}=1.273 g cm^{-3} (Z=2), D_{obsd}=1.25 g cm^{-3} (by floatation method in aqueous KI solution), μ(Mo$K\alpha$)=5.94 cm^{-1}, crystal dimension 0.5×0.4×0.3 mm, scan mode θ-2θ, scan width (1.0+0.5tanθ), 2θ range 2.5°—48°, octant collected +h, ±k, ±l, no. of unique data used 5852.

The reflection data were corrected for Lorentz-polarization effects, but not for absorption. The structure was solved by a standard heavy-atom method and refined by a block-diagonal least-squares method. The final discrepancy indices, R and R_w, are 5.79 an 5.46%, where equal weight w=1 was adopted. The calculation was carried out by a FACOM M 386 computer at thc Computer Center of Kyushu University using the UNICS III computer program system.[8] The final positional parameters of non hydrogen atoms with their estimated standard deviations in parentheses are given in Table 1.[9]

Results and Discussion

The molar electrical conductance measured in acetonitrile is 144 S mol^{-1} cm^2, consistent with 1 : 1 electrolyte.[10] This indicates that the Cl⁻ ion is coordinated to the zinc ion. The complex is diamagnetism, being consistent with the d^{10} electronic configuration of Zn(II).

A perspective drawing of the cation [Zn(Cl⁻)-(NTBEt)]⁺ with the atom numbering scheme is shown in Fig. 1. The zinc ion is coordinated by three imidazolyl nitrogen atoms of the tripod ligand NTBEt, forming a basal plane and a tertiary amine nitrogen atom N(7) and a Cl⁻ ion occupying two axial positions. The bond distances of Zn-axial ligand (Zn-Cl 2.236(1) and Zn-N(7) 2.274(4) Å) are elongated compared with those of Zn-basal plane ligand (Zn-N(1) 2.031(3), Zn-N(3) 2.056(4), and Zn-N(5) 2.046(4) Å). The geometry of the penta-coordinate metal complex can be analyzed and described by using an approach developed by Muetterties and Guggenberger.[11] In this method, the important dihedral angles (known as the shape determining angles (e_1, e_2, e_3)) can be calculated in order to describe the complex geometry. The two

Table 1. Fractional Atomic Coordinates ($\times 10^4$) of [Zn(Cl)(NTBEt)][BPh_4]·Acetone with Their Estimated Standard Deviations in Parentheses

Atom	X	Y	Z	B_{eqv}	Atom	X	Y	Z	B_{eqv}
Zn	8255(0)	−839(0)	6330(1)	4.27(1)	C26	8735(4)	271(3)	3501(5)	4.51(16)
Cl	8495(1)	119(1)	7783(1)	5.97(4)	C27	9047(4)	−904(3)	2107(5)	5.35(19)
N1	9246(3)	−1817(2)	7293(3)	3.74(11)	C28	8098(5)	−777(4)	904(6)	7.72(26)
N2	9844(3)	−3116(2)	7376(3)	3.77(11)	C29	8651(3)	−873(3)	4066(4)	3.97(14)
N3	6722(3)	−938(2)	5930(3)	3.85(11)	C30	8636(4)	−1730(3)	4101(4)	4.15(15)
N4	5226(3)	−1268(2)	4607(3)	4.10(12)	B	−2781(4)	6003(3)	11515(5)	4.21(18)
N5	8510(3)	−374(2)	4946(3)	4.10(12)	C31	−1589(4)	6205(3)	12177(4)	4.33(16)
N6	8799(3)	−524(2)	3175(4)	4.41(13)	C32	−883(4)	5967(3)	13389(4)	4.33(15)
N7	7976(3)	−1782(2)	4802(3)	3.73(11)	C33	135(4)	6114(3)	13925(5)	5.60(18)
C1	10047(3)	−1999(2)	8461(4)	3.68(14)	C34	496(4)	6509(3)	13268(6)	6.16(20)
C2	10488(4)	−1526(3)	9489(4)	4.52(16)	C35	−163(4)	6767(3)	12079(6)	6.13(22)
C3	11289(4)	−1898(3)	10524(4)	5.11(17)	C36	−1199(4)	6620(3)	11522(5)	5.34(19)
C4	11667(4)	−2717(3)	10568(5)	5.18(17)	C37	−2932(4)	5527(3)	10163(4)	4.21(15)
C5	11249(4)	−3192(3)	9557(5)	4.71(16)	C38	−2142(4)	5266(3)	9698(5)	5.07(18)
C6	10438(3)	−2816(2)	8519(4)	3.78(14)	C39	−2311(5)	4845(3)	8565(5)	6.33(23)
C7	9876(4)	−3962(2)	7087(4)	4.40(16)	C40	−3289(5)	4685(3)	7880(5)	6.70(23)
C8	9254(5)	−4285(3)	7647(6)	6.32(23)	C41	−4089(5)	4915(4)	8309(5)	6.80(22)
C9	9143(3)	−2498(2)	6681(4)	3.53(13)	C42	−3902(4)	5326(3)	9429(5)	6.07(20)
C10	8294(3)	−2551(2)	5430(4)	3.87(14)	C43	−2949(3)	5448(3)	12457(4)	4.14(15)
C11	5963(3)	−717(2)	6458(4)	3.87(14)	C44	−3142(4)	5761(3)	13519(5)	5.49(19)
C12	6046(4)	−365(3)	7618(4)	4.43(15)	C45	−3226(5)	5305(4)	14373(5)	6.78(23)
C13	5161(4)	−248(3)	7910(5)	5.35(18)	C46	−3136(5)	4511(4)	14189(5)	7.00(23)
C14	4225(4)	−463(3)	7082(5)	5.91(20)	C47	−2953(5)	4165(3)	13161(6)	6.50(22)
C15	4130(4)	−798(3)	5925(5)	5.48(18)	C48	−2860(4)	4631(3)	12314(5)	5.07(17)
C16	5026(3)	−921(3)	5645(4)	4.06(15)	C49	−3736(4)	6818(3)	11176(4)	4.46(16)
C17	4451(4)	−1552(3)	3472(4)	5.21(17)	C50	−3594(4)	7556(3)	10983(4)	4.72(16)
C18	4228(5)	−2330(4)	3656(6)	7.25(24)	C51	−4420(5)	8204(3)	10541(5)	5.95(20)
C19	6245(3)	−1271(2)	4843(4)	3.70(13)	C52	−5433(5)	8141(4)	10275(6)	7.37(24)
C20	6828(4)	−1597(3)	4009(4)	4.09(14)	C53	−5619(5)	7432(4)	10488(6)	7.59(25)
C21	8564(3)	361(3)	4610(5)	4.35(15)	C54	−4775(4)	6794(3)	10948(6)	6.35(22)
C22	8436(4)	1106(3)	5167(5)	5.23(17)	CA3	3741(5)	2834(3)	12910(6)	7.29(25)
C23	8473(4)	1737(3)	4559(6)	6.18(21)	CA1	2952(7)	2532(4)	11791(6)	9.66(34)
C24	8623(4)	1638(3)	3441(6)	6.67(23)	CA2	4637(8)	3000(6)	12761(9)	12.46(47)
C25	8776(4)	907(3)	2889(5)	5.76(20)	OA	3590(4)	2923(3)	13869(4)	7.91(17)

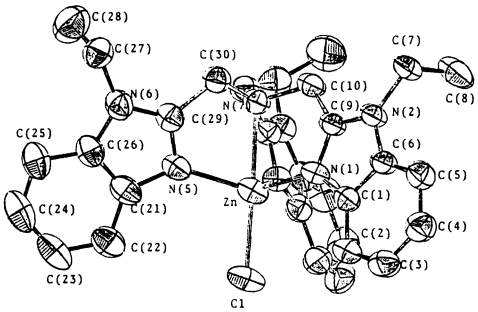

Fig. 1(a). Perspective drawing of [Zn(Cl⁻)(NTBEt)]⁺ with the atom numbering scheme.

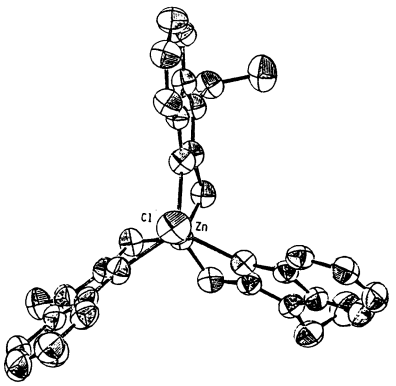

Fig. 1(b). Perspective drawing of [Zn(Cl⁻)(NTBEt)]⁺ projected along Zn-axial ligand direction.

possible limiting geometries for a penta-coordinate metal center are square-base pyramid(SP) and trigonal bipyramid(TBP) geometries. The shape-determining parameters are (e_1, e_2, e_3)=(75.7°, 75.7°, 0°) for an SP complex and (e_1, e_2, e_3)=(53.1°, 53.1°, 53.1°) for a TBP complex. As applied to the present complex **2**, the analysis yields parameters (44.9°, 46.9°, 54.9°), indicating that the coordination geometry is described as a trigonal bipyramid. On the other hand, the copper(II) sphere with the same tripod ligand NTBEt in the complex **1** has the shape determining parameters (72.0°, 63.7°, 18.5°),[4] indicating that the coordination geometry of the copper(II) sphere is an intermediate geometry between a square-base pyramid and a trigonal bipyramid. The structural difference between the zinc (II) and copper(II) sphere with the same ligand is probably attributable to their electronic configurations. The present result suggests that the molecular

structure of the metal-replaced compound of the hetero-metal polynuclear complex may be different from that the original complex.

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