

The Synthesis and Crystal Structure of Imidazolate-bridged [Cu(tren)(im)Zn(tren)](ClO₄)₃·MeOH (tren = tris(2-aminoethyl)amine; im = imidazolate)

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The reaction of [Cu(tren)](ClO₄)₂ [tren = tris(2-aminoethyl)amine] with [Zn(tren)](ClO₄)₂ and imidazole in alkaline MeOH–H₂O solution gives imidazolate-bridged [Cu(tren)(im)Zn(tren)](ClO₄)₃·MeOH (im = imidazolate) which is similar to the active centre of superoxide dismutase as shown by X-ray crystallography.

The synthesis of imidazolate-bridged Cu^{II}–Zn^{II} complexes and the study of their chemical properties are of great interest^{1,2} in relation to the active site of the enzyme bovine erythrocyte superoxide dismutase (BESOD). Because the basicities of Cu^{II} and Zn^{II} do not match well the basicity of the imidazole, and the imidazolate bridge in the complex is easily broken, it is very difficult to synthesize imidazolate-bridged heteronuclear Cu^{II}–Zn^{II} complexes and there have been few reports³ on the synthesis and X-ray structure^{4,5} of this kind of complex. We herein report the synthesis and X-ray structure of the imidazolate-bridged Cu^{II}–Zn^{II} complex [Cu(tren)(im)Zn(tren)](ClO₄)₃·MeOH [tren = tris(2-aminoethyl)amine, im = imidazolate] as a new model compound for the active centre of BESOD.

An alkaline aqueous solution (10 ml) of imidazole (1 mmol; 0.068 g) was added to a 1 : 1 mixture of [Cu(tren)](ClO₄)₂ (1 mmol; 0.408 g) and [Zn(tren)](ClO₄)₂ (1 mmol; 0.410 g) in 40 ml 50% MeOH–H₂O solution at room temperature. pH Control was essential to avoid precipitation of metal hydroxides during the reaction (pH *ca.* 10). Upon standing, light blue microcrystals precipitated in 60% yield. Blue film-shaped crystals of [Cu(tren)(im)Zn(tren)](ClO₄)₃·MeOH suitable for

X-ray diffraction were obtained on recrystallization from cold methanol–acetonitrile (1 : 1).^{†‡}

The electronic reflectance spectrum of the complex has a

[†] *Crystal data*: C₁₆H₄₃Cl₃N₁₀O₁₃CuZn, *M* = 818.27, monoclinic, space group C₂²–P2₁, *a* = 8.924(2), *b* = 11.590(4), *c* = 16.356(6) Å, β = 91.40(2)°, *U* = 1691.18(1.03) Å³, *Z* = 2, *D_c* = 1.607 g cm^{–3}. The maximum residual electron density is 0.701 and the final maximum shift over esd is 0.079. Data were measured on an R3M/E diffractometer with a graphite monochromator. Cu–Kα radiation using θ–2θ scan. A total of 1998 unique reflections were obtained in the range 3 ≤ 2θ ≤ 110°, 1676 of which with *I* ≥ 3σ(*I*) were used in the refinement. The structure was solved by direct methods. Two heavy atom peaks were first obtained; the environments around these two peaks were alike, but the electronic densities and temperature factors were different. Assuming that the peak with the larger electronic density was that of Zn, the electronic densities and temperature factors were consistent. The refinement of the structure was by full-matrix least-squares to a final *R* of 0.064. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] Satisfactory elemental analyses were obtained.

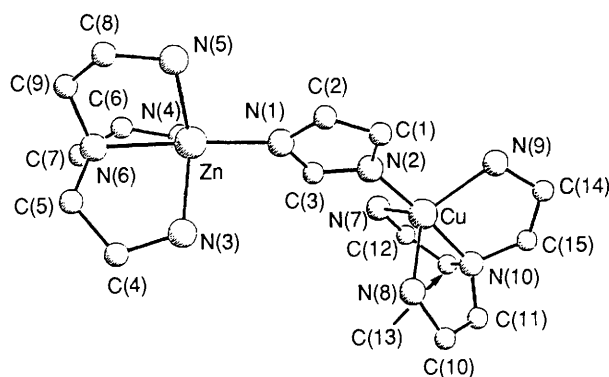


Fig. 1 The X-ray crystal structure of $[\text{Cu}(\text{tren})(\text{im})\text{Zn}(\text{tren})](\text{ClO}_4)_3$. Selected bond lengths (Å) and angles ($^\circ$): Zn–N(1) 1.964(10), Zn–N(3) 2.095(12), Zn–N(4) 2.106(12), Zn–N(5) 2.044(13), Zn–N(6) 2.057(11), Cu–N(2) 1.954(10), Cu–N(7) 2.076(17), Cu–N(8) 2.053(15), Cu–N(9) 2.075(12), Cu–N(10) 2.045(11); N(1)–Zn–N(3) 93.7(5), N(1)–Zn–N(4) 98.0(5), N(3)–Zn–N(4) 115.6(5), N(1)–Zn–N(5) 98.7(5), N(3)–Zn–N(5) 122.8(5), N(4)–Zn–N(5) 117.4(6), N(1)–Zn–N(6) 176.6(4), N(3)–Zn–N(6) 82.9(5), N(4)–Zn–N(6), 83.0(5), N(5)–Zn–N(6) 83.7(5), N(2)–Cu–N(7) 98.0(6), N(2)–Cu–N(8), 93.9(5), N(7)–Cu–N(8) 115.6(8), N(2)–Cu–N(9) 98.6(5), N(7)–Cu–N(9) 118.2(6), N(8)–Cu–N(9) 122.0(7), N(2)–Cu–N(10) 175.3(4), N(7)–Cu–N(10) 83.2(6), N(8)–Cu–N(10) 81.5(5), N(9)–Cu–N(10) 84.7(5)

maximum at $12\,300\text{ cm}^{-1}$ and a high-energy shoulder at $15\,700\text{ cm}^{-1}$. This spectrum is similar to that previously reported⁶ for $[\text{Cu}(\text{tren})\text{NH}_3]^{2+}$ and exhibits trigonal bipyramidal stereochemistry for copper. The X-band EPR spectrum of the complex in 1:1 dimethyl sulphoxide (DMSO)–methanol solution at 110 K is typical of a trigonal bipyramidal stereochemistry^{6,7} with $g_{\perp} = 2.191$ and $g_{\parallel} = 2.007$. This EPR spectrum is quite different from that of the imidazolate-bridged binuclear copper(II) complex $[\text{Cu}_2(\text{tren})_2\text{im}](\text{ClO}_4)_3$ which shows a single symmetrical derivative at $g = 2.131$.⁸

The crystal structure of the complex is shown in Fig. 1. The complex includes a bridging imidazolate ligand linking Cu and Zn (Cu–Zn 5.84 Å). The Cu is pentacoordinated by four nitrogen atoms from tren and one nitrogen atom from the bridging imidazolate ion, in an approximately trigonal bipyramidal environment. N(7), N(8), N(9) and Cu form the trigonal plane with N(2) and N(10) at the apex. The best-plane calculations reveal that Cu is 0.1846 Å below the best mean plane through N(7), N(8), N(9) and Cu, while N(7), N(8) and N(9) are 0.059, 0.062 and 0.063 Å, respectively, above that plane. These values reflect the movement of the Cu atom out of the trigonal plane towards the nitrogen atom of the bridging imidazolate ion. This movement results from the short bond

distance between the Cu atom and N(2) [Cu–N(2) 1.954 Å] of the bridging imidazolate ion, which is also seen in the imidazolate-bridged $\text{Cu}^{\text{I}}\text{–Cu}^{\text{II}}$ complex.⁹ The coordination environment of the Zn atom is similar to that of the Cu atom. The Zn is coordinated to four nitrogen atoms from tren and one nitrogen atom from the bridging imidazolate ion, so that Zn is also five-coordinate with an approximately trigonal bipyramidal geometry. N(3), N(4), N(5) and Zn form the trigonal plane with N(1) and N(6) at the apex. The Zn–N(1) bond (1.964 Å) is the shortest of the five Zn–N bonds. The atoms of the imidazolate ion all lie within 0.013 Å of the best mean plane through the ring. The Cu and Zn are 0.278 and 0.062 Å, respectively, out of the plane.

In the active site of BESOD, the Cu^{II} and Zn^{II} atoms lie 6.3 Å apart, linked by the imidazolate ring of the His-61. The Cu ligands form a distorted square-pyramid and the Zn ligand geometry is tetrahedral with strong distortion toward a trigonal pyramid.¹⁰ The ring of the bridging imidazolate is almost planar to the metals. Cu deviates from the plane by about 0.3 Å and Zn is just located in this plane.¹¹ Thus the structure of imidazolate-bridged Cu–Zn complex is similar to the active centre of BESOD.

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