A Monomeric Zinc Complex Ligated by an Unsymmetric Hydrotris(pyrazolyl)borate Containing an OH Group

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A novel zinc complex having an unsymmetric tris(pyrazolyl)borate, $Zn(OAc)[HB(3\text{-}Me_2C(OH)\text{-}5\text{-}iPrpz)(3,5\text{-}iPr_2pz)_2]$, was synthesized by the transmetalation of an oxygenated product formed a dimanganese(II, II) complex $\{[Mn[HB(3,5\text{-}iPr_2pz)_3]\}_2(OH)_2$ with molecular oxygen.

Since the original report by Trofimenko in 1966,[1] tris(pyrazolyl)borate ligand, $Tp^{R,\ R'}$ = $[HB(3\text{-}R\text{-}5\text{-}R'pz)_3]^-$ has been widely used in inorganic, organometallic, and bioinorganic chemistry.[2] Some recent improvements involve the incorporation of various bulky substituted groups into the 3- and/or 5-positions of pyrazole ring to inhibit the formation of an inert bis-chelated species and to stabilize unusual coordination structures.[3] Although unsymmetric tris(pyrazolyl)borate ligands, $[HB(pz)(pz')(pz'')]^-$ or $[HB(pz)_2(pz')]$, are expected to allow the synthesis of a new class of metal complexes particularly functioning as stereo specific catalysts, the preparation of such ligands is daunting. While there is one report,[4] it is extremely difficult to synthesize such an unsymmetric tris(pyrazolyl)borate starting from a dihydrobis(pyrazolyl)borate, mainly because of the facile intermolecular exchange of pyrazolyl groups. For instance, the reaction of $K[H_2B(3,5\text{-}iPr_2pz)_2]$ with $3,5\text{-}Ph_2pzH$ gave only the mixture of symmetric hydrotris(pyrazolyl)borates, $K[HB(3,5\text{-}iPr_2pz)_3]$ and $K[HB(3,5\text{-}Ph_2pz)_3]$.[5,6]

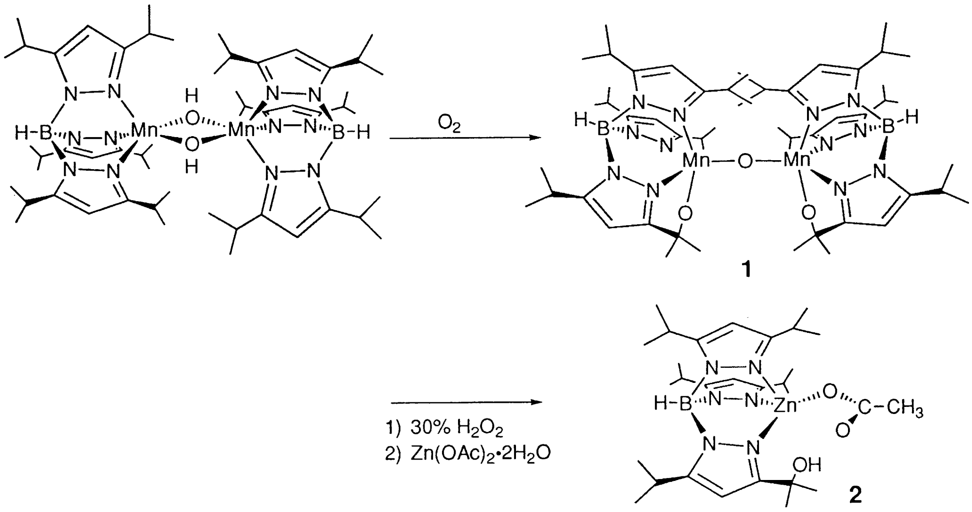
Recently, we have reported the dioxygenase type ligand oxidation in a dimanganese complex with molecular oxygen in which both atoms of dioxygen are incorporated into the CH bonds of isopropyl groups to generate a μ-oxo dimanganese (III, III) complex (**1**).[7] (Scheme 1) This ligand oxidation provides us with a useful method to prepare a novel unsymmetric tris(pyrazolyl)borate ligand. Thus , we reduced manganese(III) ion in **1** to manganese(II) ion with H_2O_2 and replaced manganese(II) ion with Zinc(II) ion which is in the highly rank of Irving-Williams' order. The blue solution of **1**(0.21 g, 0.19 mmol) was stirred with 30% H_2O_2 aq. (0.38 ml, 3.86 mmol) for 10 min in toluene. During this reaction the color of the solution changed to colorless. To this solution was added $Zn(OAc)_2{\cdot}2H_2O$(0.09 g, 0.40 mmol) and the mixture was vigorously stirred for 2 hours. The resultant brown precipitate was removed by filtration over Celite, and the colorless filtrate was evaporated to dryness under vacuum. Recrystallization of the solid from MeCN afforded $Zn(OAc)[HB(3\text{-}Me_2C(OH)\text{-}5\text{-}iPrpz)(3,5\text{-}iPr_2pz)_2]$(**2**)[8] as colorless crystals in 60% yield.[9] The existence of an alkoxo OH group in **2** is clearly established on the basis of the following evidences; (1) The strong IR band is observed at 3456 cm^{-1} which is assigned to the ν(OH); (2) ^1H-NMR of **2** gives the signal due to the OH group at 5.93 ppm (D_2O exchangeable); (3) The alkoxy carbon is observed at 68.2 ppm by ^{13}C-NMR; (4) The FDMS spectrum of **2** exhibits a peak at 605 based on the molecular ion M^+.

The molecular structure of **2** was finally determined by X-ray crystallography and its ORTEP drawing is shown in Figure 1.[10]

A monomeric tetrahedral structure of **2** with one hydroxylated isopropyl group was definitely established. The C-O bond distance (1.37(2) Å) found in an isopropyl group is consistent with identification of the alkoxo formation. The molecule sits on a crystallographically imposed mirror plane consisting of a pyrazole ring, boron, zinc, and the acetate. Since the Zn-O2 bond distance (2.398(7) Å) is considerably more elongated than Zn-O1, the coordination mode of the acetate can be described as either monodentate or highly distorted bidentate. This is consistent with the IR data which exhibits a strong ν_a(COO) band at 1601 cm^{-1} diagnostic of a monodentate acetate.[11]

Complex **2** possesses a non-coordinating alkoxo OH group which can be functioned. Thus, synthetic endeavors to connect

Scheme 1.



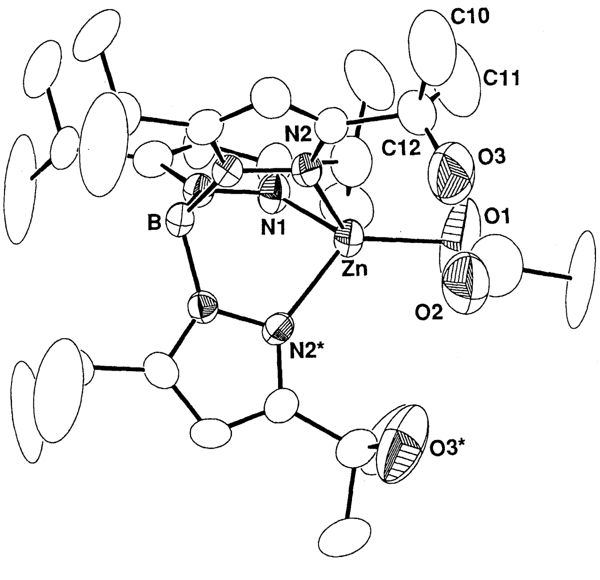


Figure 1. ORTEP view of Zn(OAc)[HB(3-$Me_2C(OH)$-5-iPrpz)(3,5-$iPr_2pz)_2$](**2**). Selected bond distances (Å) and angles (deg): Zn-O1, 2.031(8); Zn-N1, 2.045(8); Zn-N2, 2.020(5); C10-C12, 1.53(1); C11-C12,1.44(2); C12-O3,1.37(2); O1-Zn-N1, 113.1(3); O1-Zn-N2, 127.4(2); O3-C12-C10, 98(1); O3-C12-C11, 120(1);C10-C12-C11, 98.8(9).

the unsymmetric tris(pyrazolyl)borate moiety with another ligand such as a porphrin is currently being undertaken in this laboratory.

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References and Notes

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6 Abbreviations used: HB(3,5-$iPr_2pz)_3$, hydrotris(3,5-diisopropyl-1-pyrazolyl)borate; 3,5-Ph_2pzH, 3,5-diphenylpyrazole; OAc, acetate.

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8 Anal Calcd for $C_{29}H_{49}N_6O_3BZn$: C, 57.48; H, 8.15; N, 13.87%; Found: C, 57.87; H, 8.27; N, 14.20%. FTIR (KBr, cm^{-1}): ν(OH) 3456, ν(BH), 2549, ν(COO) 1601, 1135. FDMS(m/z): 605 (M^+). ^{1}H-NMR (C_6D_6, δ, ppm): 1.10(s, 6H, C(OH)Me_2), 1.15(d, 12H, CHMe_2), 1.21(d, 6H, CHMe_2), 1.25(d, 12H, CHMe_2), 1.66(s, 3H, OOCMe), 3.54(m, 3H, C$H$$Me_2$), 3.70(m, 2H, C$H$$Me_2$), 5.82(s, 1H, pz-4-H), 5.84(s, 2H, pz-4-H), 5.93(s, 1H, C(OH)Me_2). ^{13}C-NMR(C_6D_6, δ, ppm): 23.0(OOCMe), 23.3(CHMe_2), 23.4(CHMe_2), 23.5(CHMe_2), 23.6(C(OH)Me_2), 26.5 (CHMe_2), 27.3(CHMe_2), 27.4(CHMe_2), 68.2(C(OH)Me_2), 97.9(Pz-C-H), 98.0(pz-C-H), 98.6(pz-C-H), 156.1(pz-C=N), 156.3(pz-C=N), 160.8(pz-C=N), 161.0(pz-C=N), 161.8(OOCMe).

9 With $Co(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)$[HB(3-$Me_2C(OH)$-5-iPrpz)(3,5-$iPr_2pz)_2$] was obtained in the same manner. Anal Calcd for $C_{27}H_{46}N_7O_4BCo$: C, 52.87; H, 7.54; N, 16.49%; Found: C, 53.33; H, 7.70; N, 16.28%. FTIR (KBr, cm^{-1}): ν(OH) 3461, ν(BH), 2544, ν(COO) 1592, 1138. FDMS(m/z): 603 (M^+).

10 Crystal data for **2** (Mw, 605.94). **2** crystallized in the orthorhombic space group. *Pnma* with a=21.229(2) Å, b=16.600(3) Å, c=9.641(3) Å, V=3397(2) Å^3, z=4 Dc=1.185 g/cm^3, μ(Mo Kα) 7.59 cm^{-1}. A Rigaku AFC5R diffractometer(Mo Kα=0.71069 Å) was used in the ω-2θ scan mode to collect 4381 unique reflections($5° < 2\theta < 55°$), of which 1765 reflections with $I \geq 3\sigma(I)$ were used in the solution and refinement. The structure was solved by the direct methods(SAPI91) and refined by the block-diagonal least-squares techniques by TEXSAN. The occupancy of the OH group was calculated as 50%. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The $R(Rw)$ factor is 7.33%(6.75%).

11 K. Nakamoto, in "Infrared and Raman Spectra of Inorganic and Coordination Compounds" 4th ed.; John Wiley & Sons: New York (1986).