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A Monomeric Side-On Peroxo Manganese(III) Complex: $\mathrm{Mn(O_2)(3,5\text{-}iPr_2pzH)(HB(3,5\text{-}iPr_2pz)_3)}$

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Manganese−dioxygen complexes are suggested to play indispensable roles in physiologically important enzymatic reactions including superoxide dismutation, decomposition of hydrogen peroxide, and dioxygen evolution from water catalyzed by manganese-containing proteins.[1] Accordingly, the characterization of structurally well-defined manganese−dioxygen complexes is of importance in current bioinorganic chemistry. To date, however, only three X-ray structures of such complexes have been reported: a monomeric side-on Mn(III) porphyrin,[2] a cis-μ-peroxo Mn(IV,IV),[3] and a μ_3-oxo μ-peroxo Mn(III,III,III) complex.[4] We now report a novel monomeric side-on peroxo complex, which forms two isomeric structures, depending upon the temperature and solvent. Both of the X-ray structures have been determined.

When bis(μ-hydroxo) dimanganese(II,II) complex $\mathrm{[Mn(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)_2}$ (**1**) was reacted with 1 equiv of H_2O_2 at room temperature, the only product isolated was a dimanganese(III,III) complex, $\mathrm{[Mn(HB(3,5\text{-}iPr_2pz)_3)]_2(O)_2}$ (**2**), as we reported previously.[5,6] However, when this reaction was carried out with excess H_2O_2 (10−20 equiv) in the presence of $\mathrm{3,5\text{-}iPr_2pzH}$ (2 equiv) at room temperature for 0.5 h, a color change of the solution to tan brown was noted. Recrystallization conducted at −20 °C from acetonitrile gave dark brown crystalline solids, which were found to contain a peroxo complex (vide infra) formulated as $\mathrm{Mn(O_2)(3,5\text{-}iPr_2pzH)(HB(3,5\text{-}iPr_2pz)_3)}$ (**3**).[7] Complex **3** is thermally unstable and decomposes slowly at room temperature in solution. We noted that a solution of **3** in diethyl ether or toluene changed its color reversibly in the range from −78 to −20 °C; the higher temperature results in a more brownish color, whereas the color is dark blue at −78 °C. This thermochromic property is evident in Figure 1, which presents the visible spectra of **3** recorded at −20 and −78 °C in toluene. Whereas the spectrum obtained at −20 °C shows a shoulder at ca. 560 nm, a characteristic band was observed at 583 nm at −78 °C. The blue crystals of **3** were successfully obtained from a dark greenish brown solution of **3** prepared with a mixture of acetonitrile, diethyl ether, and pentane at −20 °C. The molecular structures of these isomers of **3** were determined by X-ray crystallography.[8] Their perspective views are presented in Figure 2, which clearly establishes that **3** is a monomeric six-coordinate side-on peroxo Mn(III) complex with coordination of $\mathrm{3,5\text{-}iPr_2pzH}$.[9]

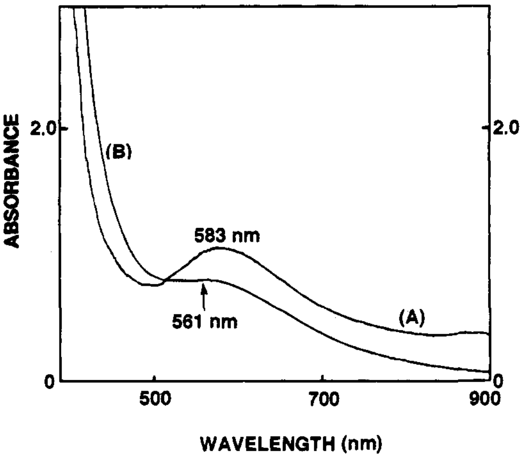

Figure 1. Visible spectra of **3** recorded at −78 °C (A) and at −20 °C (B) in toluene (15.4 mM **3**; cell path length, 1 cm). Spectrum A was recorded first, and the temperature was elevated to −20 °C, giving spectrum B. When the solution was recooled to −78 °C, the spectrum was identical to A.

The O−O distances found in the brown and blue forms of **3** are both 1.43 Å, which is typical for a peroxide ion bound to a transition metal ion.[10] Both crystalline samples exhibit a sharp characteristic IR band at 892 cm^{-1}, which is assignable to ν(OO), coinciding with this identification.[11] In each structure, $\mathrm{3,5\text{-}iPr_2pzH}$ (not pyrazolate based on IR) occupies a sixth coordination site, constructing a very distorted octahedron around the manganese with a N_4O_2 ligand donor set. The N21 and N41 atoms serve as apical ligands. A similar six-coordinate side-on peroxo Mn(III) complex with N_4O_2 ligand donors is known with a porphyrin ligand.[2] The structural features of the $Mn-O_2$ moiety adopted in **3** are very close to those seen in the porphyrinato complex. However, the overall coordination environment is clearly distinctive; that of the porphyrin complex is best described as square-pyramidal if the peroxide is regarded as a monoligand, whereas that of **3** is trigonal-bipyramidal. While the overall molecular structures of the brown and blue isomers are very similar, the distinct features that are notable are the bond distances between the oxygen atoms of the peroxide and a nitrogen from 3,5-diisopropylpyrazole. In the brown form, the O−N distances are 3.083(3) and 3.298(8) Å, which are too long to indicate a hydrogen bond. In the blue isomer, however, the O−N distances are shorter; in particular, the length of O2−N42 (2.82(2) Å) is located in the range for the distances expected for a hydrogen bond between the peroxide and the pyrazole

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[5] Abbreviations used: $\mathrm{HB(3,5\text{-}iPr_2pz)_3}$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate; $\mathrm{3,5\text{-}iPr_2pzH}$ = 3,5-diisopropylpyrazole.

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[7] The brown crystals were isolated in 54% yield. Anal. Calcd for **3** ($C_{36}H_{62}N_8O_2BMn$): C, 61.36; H, 8.87; N, 15.90. Found: C, 61.53; H, 9.02; N, 16.13. IR (KBr, cm^{-1}): ν(NH), 3374; ν(CH of pzH), 3118; ν(BH), 2535; ν(OO), 892. The blue form was isolated in 56% yield. Anal. Found: C, 61.27; H, 9.45; N, 16.19. IR (KBr, cm^{-1}): ν(NH), 3317−3334; ν(BH), 2544; ν(OO), 892.

[8] The brown form of **3** (fw = 704.69) crystallized in the orthorhombic space group $Pna2_1$ with $a = 22.539(5)$ Å, $b = 12.335(4)$ Å, $c = 14.494(4)$ Å, $V = 4030(3)$ Å^3, $Z = 4$, and $D_{calcd} = 1.16$ g cm^{-3}. The R (R_w) factor is 4.5% (5.4%) for 2182 observed reflections ($2\theta_{max} = 45°$, $I > 3\sigma(I)$) collected at −70 °C. The blue form crystallized in the monoclinic space group $P2_1/c$ with $a = 21.511(3)$ Å, $b = 9.869(3)$ Å, $c = 19.691(5)$ Å, $\beta = 101.27(2)°$, $V = 4099(3)$, $Z = 4$, and $D_{calcd} = 1.14$ g cm^{-3}. Unfortunately, the size of the crystal obtained was small, which caused the relatively low quality of the data and refinement. Accordingly, the location of the hydrogen atom on N42 could not be determined. The current R (R_w) factor is 7.2% (7.5%) for 2003 observed reflections ($2\theta_{max} = 45°$; $I > 3\sigma(I)$) recorded at −80 °C.

[9] A side-on superoxocobalt(II) complex with a similar hindered hydrotris(pyrazolyl)borate has been reported: Egan, J. W., Jr.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445.

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[11] The assignment was confirmed by labeling experiments: $\nu(^{18}O^{18}O)$, 841 cm^{-1}. While the ν(OO) is expected to vary in the brown and blue forms, experimentally the wavenumber was identical. Further detailed spectroscopic and MO explorations must be undertaken to account for this surprising observation.

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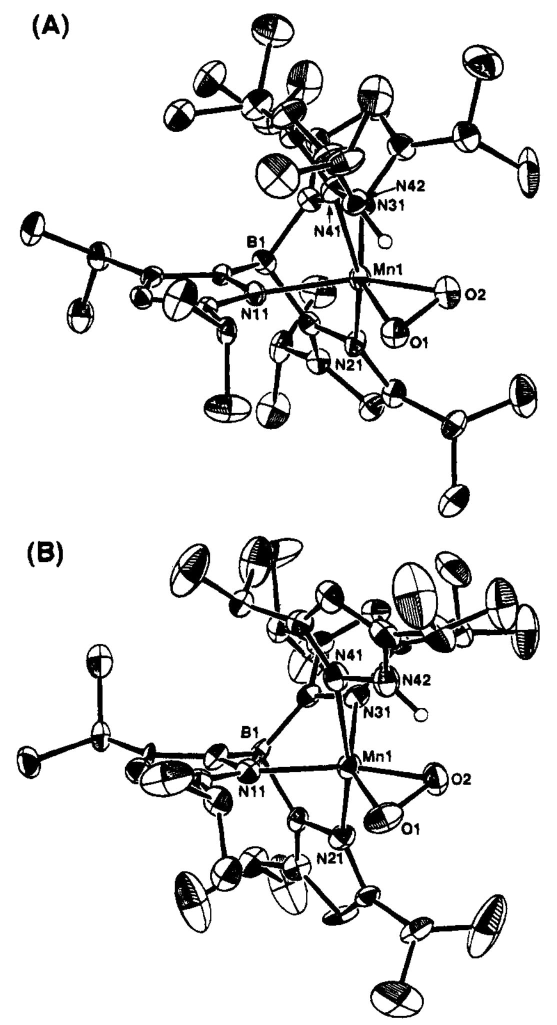

Figure 2. Perspective views of the brown (A) and blue (B) isomers of **3**. Selected bond distances (Å) and angles (deg) for A: Mn1−O1, 1.851(5); Mn1−O2, 1.850(6); Mn1−N11, 2.067(5); Mn1−N21, 2.270(6); Mn1−N31, 2.066(6); Mn1−N41, 2.406(6); O1−O2, 1.428(7); N21−Mn1−N41, 160.3. For B: Mn1−O1, 1.841(9); Mn1−O2, 1.878(8); Mn1−N11, 2.09(1); Mn1−N21, 2.24(1); Mn−N31, 2.04(1); Mn−N41, 2.41(1); O1−O2, 1.43(1); N21−Mn1−N41, 166.1(1).

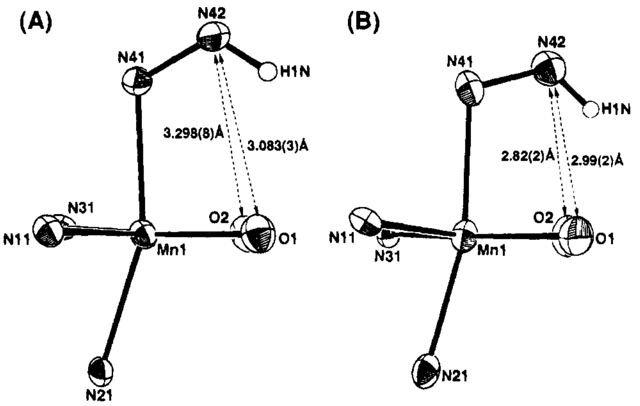

Figure 3. ORTEP views of the $N_3Mn(O_2)(N{-}\mathit{NH})$ moieties of the brown (A) and blue (B) isomers. The hydrogen atom in the brown form of **3** was found in the Fourier difference map and refined isotropically, whereas the position of the one in the blue isomer could not be located because of the relatively low refinement; thus in this case, the position of the hydrogen was calculated with an N−H distance of 0.95 Å and an N−N−H angle of 120°. Each hydrogen atom is represented as a ball with an isotropic thermal parameter of 1.0 Å^2. Selected bond distances (Å) and angles (deg) for A: O1−N42, 3.083(3); O2−N42, 3.298(8); N41−N42, 1.368(8); Mn1−O1−O2, 67.3(3); Mn1−O2−O1, 67.3(3); O1−Mn1−O2, 45.4(2); Mn1−N41−N42, 114.6(4). For B: O1−N42, 2.99(2); O2−N42, 2.82(2); N41−N42, 1.36(1); Mn1−O1−O2, 68.8(5); Mn1−O2−O1, 66.0(5); O1−Mn1−O2, 45.2(4); Mn1−N41−N42, 108.0(9).

proton. This is evident in Figure 3, where the expanded views of the $N_3Mn(O_2)(N{-}\mathit{NH})$ moieties of brown and blue forms are compared. In accord with the existence of the hydrogen bond between O2 and the proton on N42 in the blue isomer, the Mn1−O2 distance is more elongated than that of Mn1−O1, whereas in the brown form, the distances are identical. Moreover, the pyrazole is forced closer to the peroxide, which causes, for instance, the smaller Mn1−N41−N42 angle.

The presence of the hydrogen bond in the blue form of **3** is consistent with the IR spectrum, which exhibits a broad band centered at ca. 3325 cm^{-1} assigned to the ν(NH) of a hydrogen-bonding pyrazole.[12] In contrast, a sharp band attributable to ν(NH) is observed at 3374 cm^{-1} for the brown form, diagnostic of a non-hydrogen-bonding pyrazole.[13] The thermochromism of **3** is, therefore, ascribed to the construction of the hydrogen bond between the pyrazole proton and the peroxide which occurs predominantly at low temperature (< -50 °C). The property seems to be associated with the polarity of the solvent as well, although more detailed investigation remains to be completed to lead to a conclusion. The hydrogen bond between the coordinated dioxygen and histidine is known to occur in myoglobin and hemoglobin.[14,15] However, to our knowledge, the present system is the first synthetic example definitely proving the presence of such an interaction.

The spontaneous decomposition of **3** in diethyl ether at room temperature resulted in formation of **2** almost quantitatively, while the mechanism has not been clarified yet. A preliminary investigation on the reactivity of **3** indicated that the oxo-transfer capability of **3** is not markedly high, rather comparable to those known for μ-peroxo copper and porphyrinato iron complexes.[16] Anaerobic oxidations of PPh_3, MeSMe, and MeS(O)Me with **3** have been tested at −78 °C and at room temperature (a mixture of **3** and the substrate prepared at −78 °C was warmed to room temperature). In both cases, $OPPh_3$ and $MeS(O)_2Me$ were formed in low yield (ca. 20% and 5% based on **3**, respectively), while MeSMe was not oxidized.

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Supplementary Material Available: Crystallographic data for the brown and blue forms of $Mn(O_2)(3,5\text{-}iPr_2pzH)(HB(3,5\text{-}iPr_2pz)_3)$ and tables of atomic parameters, anisotropic thermal parameters, bond lengths, and bond angles (17 pages); observed and calculated structure factors (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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