1782 *Inorg. Chem.* **1997,** *36,* 1782−1785

Synthesis and Structural Characterization of Five-, Six-, and Seven-Coordinate Manganese(II) Complexes of the Tripodal Ligand Tris(2-benzimidazolylmethyl)amine

Myoung Soo Lah* and Hyungphil Chun

Department of Chemistry, College of Science, Hanyang University,
1271 Sa-1-dong, Ansan, Kyunggi-do 425-791, Korea

Received August 2, 1996⊗

A series of manganese(II) tris(2-benzimidazolylmethyl)amine (ntb) complexes were synthesized and characterized. In these complexes, ntb functions as a tripodal tetradentate ligand, resulting in trigonal pyramidal geometry. The complexes have five- to seven-coordinate manganese(II) ions depending on the additional ligand used. In each complex, an additional ligand, chloride anion, acetate anion, or nitrite anion, is coordinated at the "opened" site trans to the apical tertiary nitrogen atom of the ntb ligand. Complex **1**, $Mn^{II}(ntb)Cl]Cl$, has trigonal bipyramidal geometry. This geometry, corresponding to the active-site geometry of native manganese superoxide dismutase, was easily constructed using ntb as a tetradentate ligand and chloride as a monodentate ligand. Complex **2**, $[Mn^{II}(ntb)(OAc)]Cl$, was synthesized using ntb as a tetradentate ligand and acetate as a chelating bidentate ligand. The seven-coordinate complex $[Mn^{II}(ntb)(NO_2)_2]$, **3**, was also synthesized using ntb as a tetradentate ligand and nitrites as both monodentate and bidentate ligands. In each case, up to three donor atoms could be accommodated by the "opened" site without significant disturbance to the trigonal pyramidal portion of the complex. Crystal data are as follows. $[Mn^{II}(ntb)Cl]Cl\cdot 2.5MeOH$, **1**: triclinic space group $P\bar{1}$; $a = 13.388(2)$ Å, $b = 14.427(2)$ Å, $c = 17.595(3)$ Å; $\alpha = 79.13(1)°$, $\beta = 83.28(2)°$, $\gamma = 66.02(2)°$; $V = 3046.3(8)$ Å^3; $Z = 4$; R1 = 0.0786, wR2 = 0.2063 for reflections of $I > 2\sigma(I)$. $[Mn^{II}(ntb)(OAc)]Cl\cdot 0.5MeOH\cdot 3.25H_2O$, **2**: triclinic space group $P\bar{1}$; $a = 13.308(1)$ Å, $b = 14.689(2)$ Å, $c = 18.335(2)$ Å; $\alpha = 75.48(1)°$, $\beta = 79.21(1)°$, $\gamma = 62.99(1)°$; $V = 3195.7(6)$ Å^3; $Z = 4$; R1 = 0.0899, wR2 = 0.2594 for reflections of $I > 2\sigma(I)$. $[Mn^{II}(ntb)(NO_2)_2]\cdot 4MeOH$, **3**: monoclinic space group $P2_1/n$; $a = 14.484(14)$ Å, $b = 15.454(14)$ Å, $c = 14.925(11)$ Å; $\beta = 114.86(6)°$; $V = 3031(5)$ Å^3; $Z = 4$; R1 = 0.0748, wR2 = 0.1614 for reflections of $I > 2\sigma(I)$.

Introduction

It is well-known that manganese plays an important role in many biological systems including photosystem II (water oxidation), catalase (disproportionation of the hydrogen peroxide), and superoxide dismutase (dismutation of the superoxide radical).[1−3] The active site of catalase contains a dinuclear manganese center,[4] whereas the tetranuclear manganese center[5] or dimer of dimers[6] serves as a current working model for the active site of photosystem II. Mononuclear and trinuclear arrangements of the manganese ions in photosystem II have also been proposed on the basis of the low-field EPR signal,[7,8] and it is now known that the mononuclear manganese center of the manganese superoxide dismutase active site has trigonal bipyramidal geometry.[9,10] While the preparation and characterization of the polynuclear manganese complex relevant to the active center of photosystem II and catalase have been studied extensively,[11−13] relatively simple mononuclear centers have received much less attention. Therefore, the synthesis and characterization of mononuclear manganese centers with biologically relevant heteroatomic donor ligands and their geometry is an important area of investigation. In this study, we describe the synthesis and characterization of various manganese(II) complexes with the tripodal tetradentate ligand tris(2-benzimidazolylmethyl)amine (ntb).

Experimental Section

Materials. The following were used as received with no further purification: tris(2-benzimidazolylmethyl)amine (Aldrich), sodium nitrite (Aldrich), manganese chloride tetrahydrate (Yakuri), manganese acetate tetrahydrate (Yakuri), and methanol (Carlo Erba).

Elemental Analyses. C, H, N, and Mn determinations were performed by the elemental analysis laboratory of the Korean Institute of Basic Science and by Galbraith Laboratory.

IR Spectroscopy. Infrared spectra were recorded as KBr pellets in the range 4000−400 cm^{-1} on a Digi Lab FT-IR spectrometer.

Mass Spectrometry. Positive-ion FAB mass spectra were obtained using a JEOL HX110A/HX110A Tandem mass spectrometer in a 3-nitrobenzyl alcohol matrix.

Electrochemistry. Cyclic voltammograms were obtained using a BAS-100A electrochemical analyzer with Ag wire as reference and a platinum working electrode with 0.1 M tetrabutylammonium chloride in DMSO.

Magnetic Susceptibility Measurements. Room-temperature magnetic susceptibilities of well-ground solid samples were measured by

---

⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) Pecoraro, V. L., Ed. *Manganese Redox Enzymes*; VCH: New York, 1992.

(2) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153−1172.

(3) Pecoraro, V. L.; Baldwin, M. J.; Gelasco, A. *Chem. Rev.* **1994**, *94*, 807.

(4) Penner-Hahn, T. E. In *Manganese Redox Enzymes*; Pecoraro, V. L., Ed. VCH: New York, 1992; p 29.

(5) Zheng, M.; Dismukes, G. C. *Inorg. Chem.* **1996**, *35*, 3307.

(6) Brid, R. D. In *Oxygenic Photosynthesis: The Light Reaction*; Ort, D. R., Yocum, C. F., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1996; p 137.

(7) Penner-Hahn, T. E.; Fronko, R.; Pecoraro, V. L.; Bowlby, N. F.; Betts, S. D.; Yocum, C. F. *J. Am. Chem. Soc.* **1990**, *112*, 2549.

(8) Hanson, Ö.; Aasa, R.; Vänngaard, T. *Biophys. J.* **1987**, *51*, 825.

(9) Lah, M. S.; Dixon, M. M.; Pattridge, K. A.; Stallings, W. C.; Fee, J. A.; Ludwig, M. L. *Biochemistry* **1995**, *34*, 1646.

(10) Tierney, D. L.; Fee, J. A.; Ludwig, M. L.; Penner-Hahn, J. E. *Biochemistry* **1995**, *34*, 1661−1668.

(11) Randall, D. W.; Sturgeon, B. E.; Ball, J. A.; Lorigan, G. A.; Chan, M. K.; Klein, M. P.; Armstrong, W. H.; Britt, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 11780.

(12) Baldwin, M. J.; Kampf, J. W.; Kirk, M. L.; Pecoraro, V. L. *Inorg. Chem.* **1995**, *34*, 5252.

(13) Sauer, K.; Yachandra, V. K.; Britt, R. D.; Klein, M. P. In *Manganese Redox Enzymes*; Pecoraro, V. L., Ed.; VCH: New York, 1992.

S0020-1669(96)00923-8 CCC: $14.00

using an Evans balance. The measurements were calibrated against a $Hg[Co(SCN)_4]$ standard.

Syntheses. (a) $[Mn^{II}(ntb)Cl]Cl$, 1. A 0.407 g (1 mmol) sample of tris(2-benzimidazolylmethyl)amine was dissolved in 25 mL of methanol, and 0.197 g (1 mmol) of manganese(II) chloride tetrahydrate was dissolved using a minimal amount of methanol in another flask. The two solutions were mixed and stirred. After 3 min of stirring, the combined solution was filtered. After slow evaporation of the filtrate solution for 1 week, pale yellowish pink rectangular crystals suitable for crystallographic study were obtained (0.48 g, 84% yield). Anal. Calcd for $[Mn(ntb)Cl]Cl\cdot 2H_2O$ ($MnC_{24}H_{25}N_7O_2Cl_2$): C, 50.63; H, 4.43; N, 17.22; Mn, 9.65. Found: C, 50.27; H, 4.00; N, 17.03; Mn, 9.55. FAB (fast atom bombardment) MS, *m/z*: $[Mn(ntb)Cl]^+$, 497.1. μ_{eff}: 5.83 μ_B.

(b) $[Mn^{II}(ntb)(OAc)]Cl$, 2. A 0.200 g (0.5 mmol) sample of tris(2-benzimidazolylmethyl)amine was dissolved in 20 mL of methanol, and 0.100 g (0.5 mmol) of manganese(II) chloride tetrahydrate was added to the solution. A 0.100 g (2.5 mmol) amount of sodium acetate was also dissolved in 20 mL of methanol in another flask. The two solutions were mixed and stirred. After 3 min of stirring the solution was filtered. After slow evaporation of the filtrate solution for 1 week, pale brown rectangular crystals suitable for crystallographic study were obtained (0.17 g, 56% yield). Anal. Calcd for $[Mn(ntb)(OAc)]Cl\cdot 3H_2O$ ($MnC_{26}H_{30}N_7O_5Cl$): C, 51.11; H, 4.95; N, 16.05; Mn, 8.99. Found: C, 50.86; H, 5.05; N, 15.72; Mn, 9.45. IR: 1560, 1407 cm^{-1} (OAc^-). μ_{eff}: 5.90 μ_B.

(c) $Mn^{II}(ntb)(NO_2)_2$, 3. A 0.20 g (0.35 mmol) sample of complex **1** was dissolved in 10 mL of methanol, and 0.20 g (3 mmol) of $NaNO_2$ was dissolved in 10 mL of methanol in another flask. After the two solutions were mixed, a small amount of fine yellowish powder formed and was filtered off immediately. The filtrate was allowed to stand for 3 days, whereupon pale yellow crystals were obtained (0.13 g, 68% yield). Anal. Calcd for $[Mn(ntb)(NO_2)_2]\cdot H_2O$ ($MnC_{24}H_{23}N_7O_5$): C, 50.36; H, 4.05; N, 22.02; Mn, 9.60. Found: C, 50.01; H, 3.99; N, 21.56; Mn, 9.82. FAB MS, *m/z*: $[Mn(ntb)(NO_2)]^+$, 508.1. IR: 1235, 1205 cm^{-1} (nitro, nitrito). μ_{eff}: 5.63 μ_B.

Crystallographic Data Collection and Refinement of the Structures. Because crystals of **1**−**3** lose their solvents of crystallization within 1 min, they were mounted in glass capillaries with the mother liquor to prevent the loss of the structural solvents during data collections. Preliminary examinations and data collections were performed with Mo Kα radiation ($\lambda = 0.710\,69$ Å) on an Enraf-Nonius CAD4 computer-controlled *κ*-axis diffractometer equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrixes for data collections were obtained from least-squares refinement, using the setting angles of 25 reflections. Data were collected at room temperature using the *ω* scan technique. Three standard reflections were monitored every hour, but no intensity variations were monitored. Lorentz and polarization corrections were applied to the data; however, no corrections were made for absorption. All structures were solved by direct methods using SHELXS-86[14] and refined by full-matrix least-squares calculations with SHELXL-93.[15] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were allowed to ride on geometrically ideal positions with isotropic temperature factors 1.2 times those of the attached non-hydrogen atoms. Crystal and intensity data are given in Table 1.

Results and Discussion

The Five-Coordinate Manganese(II) Complex. $[Mn^{II}(ntb)Cl]Cl$, **1**, was synthesized using manganese(II) chloride as the metal source and tris(2-benzimidazolylmethyl)amine as a neutral tripodal tetradentate ligand. The crystal structure shows two crystallographically independent but chemically identical molecules. An ORTEP drawing of one of these molecules (complex **1**) is shown in Figure 1. Complex **1** is the same as one of the two cocrystallized but chemically different compounds previously reported where one is a monochloro pentacoordinate trigonal bipyramidal complex and the other is a *cis*-dichloro hexacoordinate distorted octahedral complex.[16] The neutral tripodal tetradentate ligand forms a trigonal pyramidal geometry with the manganese(II) ion, and the monodentate chloride anion occupies the remaining "opened" axial position to complete a trigonal bipyramidal geometry. Another chloride anion exists as a counterion. The oxidation state of the manganese ion is +2, as confirmed by room-temperature magnetic susceptibility measurements. Redox stability of complex **1** is observed in the cyclic voltammogram. The FAB mass spectrum of complex **1** showed a peak at *m/z* 497.1 for $[Mn(ntb)Cl]^+$. The bond distance between the manganese ion and the apical nitrogen atom (N(1)) is 2.510 Å, about 0.35 Å longer than the bond distances between the manganese ion and the trigonal basal nitrogen atoms (2.137−2.169 Å, average = 2.156 Å) (Table 2). This significant elongation is always observed in manganese complexes of tripodal tetradentate ligands with the benzimidazolylmethyl group.[17,18] Similar elongations are also observed in zinc complexes of analogous ligands.[18−20] However the corresponding bond distances of cobalt and iron complexes are relatively short.[18,21,22] The average bond angle (N_A−Mn−N_B)

Table 1. Crystallographic Data for $[Mn^{II}(ntb)Cl]Cl\cdot 2.5MeOH$ (**1**), $[Mn^{II}(ntb)(OAc)]Cl\cdot 0.5MeOH\cdot 3.25H_2O$ (**2**), and $[Mn^{II}(ntb)(NO_2)_2]\cdot 4MeOH$ (**3**)

	1	**2**	**3**
empirical formula	$C_{27}H_{30}Cl_2MnN_7O_{2.5}$	$C_{26.5}H_{32.5}ClMnN_7O_{5.75}$	$C_{27}H_{29}MnN_9O_6$
fw	606.41	631.49	630.53
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	13.388(2)	13.808(1)	14.484(14)
b, Å	14.427(2)	14.689(2)	15.454(14)
c, Å	17.595(3)	18.335(2)	14.925(11)
α, deg	79.13(1)	75.48(1)	
β, deg	83.28(2)	79.21(1)	114.86(6)
γ, deg	66.02(2)	62.99(1)	
V, $Å^3$	3046.3(8)	3195.7(6)	3031(5)
max *θ* value, deg	22.5	20	20
crystal size, mm	0.20 × 0.40 × 0.50	0.30 × 0.50 × 0.70	0.10 × 0.30 × 0.50
no. of reflns collected	5673	5967	2500
no. of indep reflns	5440 [$R_{int} = 0.03$]	5967 [$R_{int} = 0.00$]	2395 [$R_{int} = 0.05$]
GOF on F^2	1.065	1.077	1.027
final *R* [$I > 2\sigma(I)$]	$R1^a = 0.0786$ $wR2^b = 0.2063$	R1 = 0.0899 wR2 = 0.2594	R1 = 0.0748 wR2 = 0.1614
R (all data)	R1 = 0.1245 wR2 = 0.2383	R1 = 0.1177 wR2 = 0.2834	R1 = 0.1350 wR2 = 0.1863

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

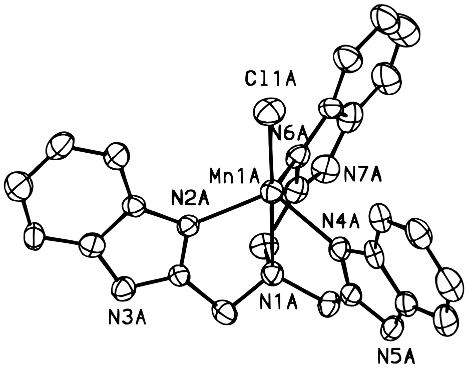

Figure 1. ORTEP drawing of the cation of complex **1**, $[Mn^{II}(ntb)Cl]^+$.

---

(14) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(15) Sheldrick, G. M. *SHELXL93*; University of Göttingen: Göttingen, Germany, 1993.

(16) Oki, A. R.; Bommarreddy, P. R.; Zhang, H.; Hosmane, N. *Inorg. Chim. Acta* **1995**, *231*, 109.

(17) Takahashi, K.; Nishida, Y.; Kida, S. *Inorg. Chim. Acta* **1983**, *77*, 1185.

(18) Takahashi, K.; Nishida, Y.; Kida, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2628.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Mn^{II}(ntb)Cl]Cl\cdot 2.5MeOH$ (**1**), $[Mn^{II}(ntb)(OAc)]Cl\cdot 0.5MeOH\cdot 3.25H_2O$ (**2**), and $[Mn^{II}(ntb)(NO_2)_2]\cdot 4MeOH$ (**3**)

	1		**2**		**3**
Mn(1)−N(6)	2.166(8)	2.154(10)	2.162(7)	2.157(9)	2.276(11)
Mn(1)−N(4)	2.149(9)	2.162(9)	2.181(6)	2.133(11)	2.201(11)
Mn(1)−N(2)	2.137(8)	2.169(10)	2.161(7)	2.169(8)	2.255(11)
Mn(1)−N(1)	2.519(8)	2.501(9)	2.535(7)	2.477(9)	2.543(9)
Mn(1)−Cl(1)	2.363(3)	2.357(4)			
Mn(1)−O(1)			2.293(7)	2.18(2)	2.321(90
Mn(1)−O(2)			2.236(8)	2.28(2)	2.317(10)
Mn(1)−O(3)					2.320(9)
N(6)−Mn(1)−N(4)	105.4(3)	112.3(3)	112.4(2)	114.8(4)	96.9(4)
N(6)−Mn(1)−N(2)	111.4(3)	107.0(4)	115.7(3)	115.0(3)	104.6(4)
N(4)−Mn(1)−N(2)	117.9(3)	117.0(4)	103.9(3)	105.0(4)	121.7(4)
N(6)−Mn(1)−N(1)	72.6(3)	73.6(3)	71.8(2)	72.7(4)	69.7(4)
N(4)−Mn(1)−N(1)	73.1(3)	73.6(3)	72.2(2)	73.1(5)	71.2(4)
N(2)−Mn(1)−N(1)	72.7(3)	72.9(3)	71.4(3)	72.6(3)	67.1(4)
N(6)−Mn(1)−Cl(1)	105.5(3)	111.0(3)			
N(4)−Mn(1)−Cl(1)	109.4(3)	105.2(3)			
N(2)−Mn(1)−Cl(1)	106.5(3)	103.9(3)			
Cl(1)−Mn(1)−N(1)	177.3(2)	175.1(3)			
O(1)−Mn(1)−N(1)			147.0(3)	155.6(10)	142.8(4)
O(2)−Mn(1)−N(1)			154.2(3)	152.6(6)	151.0(4)
O(3)−Mn(1)−N(1)					113.5(3)
N(6)−Mn(1)−O(1)			91.4(3)	98.5(9)	88.3(3)
N(4)−Mn(1)−O(1)			140.6(3)	130.2(11)	143.4(4)
N(2)−Mn(1)−O(1)			92.1(3)	91.9(6)	91.5(4)
N(6)−Mn(1)−O(2)			104.1(4)	99.4(6)	91.5(4)
N(4)−Mn(1)−O(2)			86.7(3)	87.6(6)	90.3(4)
N(2)−Mn(1)−O(2)			129.8(4)	132.5(7)	141.1(4)
N(6)−Mn(1)−O(3)					176.4(4)
N(4)−Mn(1)−O(3)					83.0(3)
N(2)−Mn(1)−O(3)					78.5(3)
O(2)−Mn(1)−O(1)			56.3(3)	49.7(9)	53.2(3)
O(3)−Mn(1)−O(1)					89.8(3)
O(2)−Mn(1)−O(3)					84.9(3)
disp[a]	0.635(5)	0.619(6)	0.675(5)	0.637(8)	0.795(7)

[a] Displacement of the Mn(II) ion from the N2−N4−N6 plane.

formed by the apical nitrogen atom (N_A), the manganese ion, and the trigonal basal nitrogen atom (N_B) is 73.1°. The manganese ion is 0.63 Å above the trigonal basal plane. The fifth ligand, the chloride anion, is coordinated at the trans position of apical nitrogen, and the bond angle N_A−Mn−Cl is 176.2°. The high-spin d^5 manganese(II) ion has no crystal field stabilization energy, so it could have various geometries depending on the coordinated ligands. However, the structure of complex **1** is one of only a few reported trigonal bipyramidal structures of the manganese(II) ion.[23]

When the weakly coordinating apical nitrogen atom is ignored, compex **1** can be described as having a pseudotetrahedral geometry with three benzimidazolyl nitrogen atoms and a chloride atom (Table 2). An isostructural pseudotetrahedral zinc(II) complex with tris((*N*-methyl-2-benzimidazolyl)methyl)amine as a pseudotridentate ligand has been reported.[18]

The Six-Coordinate Manganese(II) Complex. $[Mn^{II}(ntb)(OAc)]Cl$, **2**, was synthesized using manganese(II) chloride as the metal source, tris(2-benzimidazolylmethyl)amine as a neutral tripodal tetradentate ligand, and the acetate anion as a chelating bidentate ligand. The crystal structure shows two crystallographically independent but chemically identical molecules. An ORTEP drawing of one of these molecules (complex **2**) is shown in Figure 2. The tripodal ligand forms a trigonal pyramidal geometry with the manganese ion, and the remaining "opened" axial site of the complex is occupied by a chelating bidentate acetate anion. The complex has a six-coordinate manganese(II) geometry. Elongation of the bond distance between the manganese ion and the apical nitrogen atom is also observed (Mn(1)−N(1) bond distance 2.506 Å). The average bond angle (N_A−Mn−N_B) of the axial nitrogen atom (N_A), the manganese ion, and the trigonal basal nitrogen atom (N_B) is 72.3°, and the manganese ion is 0.66 Å above the trigonal basal plane. The average bond distance between the manganese and nitrogen atoms of complex **2** (2.247 Å) is similar to that of the five-coordinate complex **1** (2.245 Å). In complex **2**, the additional ligand is accommodated at the "opened" axial site without any significant change in the trigonal pyramidal part of the complex (average N(2)−Mn(1)−N(4) = 117.5° for complex **1** and 104.5° for complex **2**). However in the *cis*-dichloro complex Mn^{II}(tris(2-benzimidazolylmethyl)amine)Cl_2, a sixth ligand, the chloride anion, opens one site of the trigonal basal plane to form a square basal plane and changes the geometry of the complex from trigonal bipyramidal to distorted octahedral (N_B−Mn−N_B = 143.1(3)°).[16] In Mn^{II}(*N*,*N*-bis(2-benzimidazolylmethyl)-ethanolamine)$(NCS)_2$, a sixth ligand, the isothiocyanide anion, assumes the same role (N_B−Mn−N_B = 142.81(2)°).[17] Similar features have also been observed in other cobalt and iron complexes.[18,21,22] When a sixth ligand is coordinated to the metal complex of a tripodal tetradentate ligand, the geometry of the three benzimidazole nitrogen atoms changes from trigonal basal to square basal to accommodate the new ligand and the complex changes its geometry from trigonal bipyramidal to octahedral.

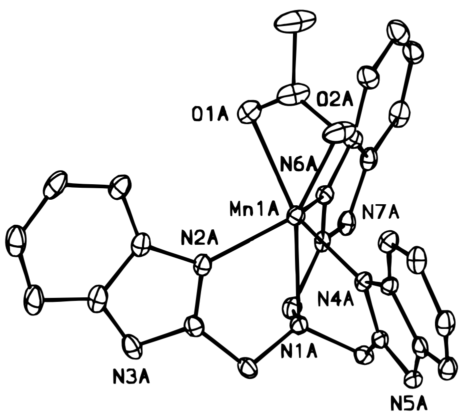

Figure 2. ORTEP drawing of the cation of complex **2**, $[Mn^{II}(ntb)(OAc)]^+$.

The Seven-Coordinate Manganese(II) Complex. The monodentate chloride was replaced by nitrite anions as shown in Figure 3. $Mn^{II}(ntb)(NO_2)_2$, **3**, was synthesized using complex **1** as starting material. When excess amounts of sodium nitrite were added to the methanol solution of complex **1**, complex **3** was obtained. Magnetic susceptibility measurements suggest that complex **3** also has a manganese(II) ion.

The tripodal ligand forms trigonal pyramidal geometry with the manganese ion in complex **3**, and the remaining "opened" axial site of the complex is occupied by both chelating bidentate and monodentate nitrite anions. The complex has a seven-coordinate manganese(II) geometry. Elongation of the bond distance between the manganese ion and the apical nitrogen atom is also observed (Mn(1)−N(1) bond distance 2.543(9) Å). The average bond angle (N_A−Mn−N_B) of the axial nitrogen

---

(19) Hartmann, U.; Gregorzik, R.; Vahrenkamp, H. *Chem. Ber.* **1994**, *127*, 2123.

(20) Gregorzik, R.; Hartmann, U.; Vahrenkamp, H. *Chem. Ber.* **1994**, *127*, 2117.

(21) Buchanan, R. M.; O'Brien, R. J.; Richardson, J. F.; Latour, J.-M. *Inorg. Chim. Acta* **1993**, *214*, 33.

(22) Wang, S.; Luo, Q.; Wang, X.; Wang, L.; Yu, K. *J. Chem. Soc., Dalton Trans.* **1995**, 2045.

(23) Phillips, F. L.; Shreeve, F. M.; Skapski, A. C. *Acta Crystallogr.* **1976**, *B32*, 687.

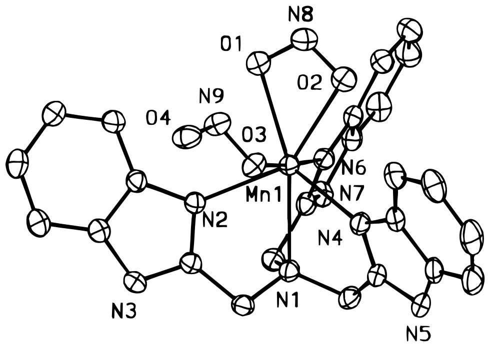

Figure 3. ORTEP drawing of complex **3**, $Mn^{II}(ntb)(NO_2)_2$.

atom (N_A), the manganese ion, and the trigonal basal nitrogen atom (N_B) is 69.3°, and the manganese ion is 0.795(7) Å above the trigonal basal plane. The average bond distance between the manganese and nitrogen atoms of complex **3** (2.319 Å) is about 0.07 Å longer than that of the five-coordinate complex **1** (Table 2). The two nitrite anions are coordinated at the "opened" site, one as a chelating bidentate nitro group and the other as a monodentate nitrito group. The oxygen atom of the monodentate nitrito group is coordinated to the trans position of the basal N(2) atom (N(2)−Mn(1)−O(3) = 176.4(4)°). The oxygen atoms of the chelating bidentate nitro group are coordinated to the approximate trans positions of the remaining two basal nitrogen atoms (N(4)−Mn1(1)−O(1) = 143.4(4)°; N(2)−Mn(1)−O(2) = 141.1(4)°). In complex **3**, all additional ligands are accommodated at the "opened" axial site without significant change in the trigonal pyramidal part of the complex (N(2)−Mn(1)−N(4) = 121.7(4)°). The steric crowding of ligands is avoided because the manganese(II) ion is slightly above the trigonal basal plane (Table 2). The space-filling model of complex **3** shows that up to three donor atoms can be accommodated in the "opened" site without significant disturbance of the trigonal pyramidal part of the structure.

The manganese(II) complexes of the tripodal ligand tris(2-benzimidazolylmethyl)amine have various geometries depending on the additional coordinated ligands. In the presence of chloride anions, the complexes have either trigonal bipyramidal geometry or distorted octahedral geometry. Even both geometries were observed in a single crystal.[16] In the presence of bidentate acetate or nitrite anions, the complexes have a trigonal pyramidal partial geometry with additional ligands coordinated at the trans "opened" site. Iron(III) complexes, however, prefer distorted octahedral geometry.[21,22] The dinuclear iron(III) complex $[Fe^{III}_2(ntb)_2OCl_2]^{2+}$ has distorted octahedral iron centers. Complexes of the tripodal ligand tris(2-benzimidazolylmethyl)amine have various geometries depending on the metal used and the additional ligands coordinated.

Acknowledgment. We thank Professor M. H. Pyo for electrochemical experiments, the Korean Institute of Basic Science for elemental analyses and mass spectra, and the National Institute of Technology and Quality for the use of an X-ray diffractometer. Ths work was supported by Grant No. BSRI-96-3443 from the Basic Research Institute Program, Ministry of Education, Republic of Korea.

Supporting Information Available: Tables giving the atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic thermal parameters of non-hydrogen atoms and atomic coordinates of hydrogen atoms and ORTEP drawings with complete atomic numbering for **1**−**3** (28 pages). Ordering information is given on any current masthead page.

IC960923O