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Mononuclear manganese carboxylate complexes: Synthesis and structural studies

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Abstract

Several manganese carboxylates complexes having $Pz^{iPr2}H$ (3,5-diisopropylpyrazole), $Tp^{Ph,Me}$ (hydrotris(3-phenyl,5-methyl-pyrazol-1-yl)borate), Tp^{ipr2} (hydrotris(3,5-diisopropyl-pyrazol-1-yl)borate) as supporting ligands have been synthesised and structurally characterized. Single-crystal X-ray diffraction studies suggest that the manganese center in complexes $(Pz^{iPr2}H)_4Mn(NO_2–OBz)_2$ (**5**) and $(Pz^{iPr2}H)_4Mn(F–OBz)_2$ (**6**) have same coordination environment and geometry whereas the complex $[Tp^{Ph,Me}Mn(OAc)Pz^{Ph,Me}H]$ (**7**) has a five coordinate manganese center. In all these complexes, the carboxylate groups are coordinated as monodentate and the uncoordinated oxygen atom of the carboxylate groups form intramolecular hydrogen bonds with the NH group of the corresponding coordinated pyrazole ($Pz^{iPr2}H/Pz^{Ph,Me}H$). The complexes **5**–**8** and **10** were tested for their superoxide dismutase activity and it was found that only complex **7** has SOD activity as its structure is very similar to the active site structure of the native Mn–SOD enzyme. The SOD activity studies on these carboxylate complexes suggest that any model compound with analogous active site structure and intramolecular hydrogen bonding may be a suitable mimic for the Mn–SOD enzyme.

Keywords: Pyrazole ligand; Carboxylate ligand; Manganese; SOD; Crystal structure

1. Introduction

Manganese is an important transition metal, required for the growth and survival of many living organisms. There are many enzymes that not only need manganese specifically but utilize its redox capabilities also. These are manganese superoxide dismutase (MnSOD) [1], manganese peroxidase (MnP) [2], manganese thiosulfate oxidase [3], manganese catalase [4], ribonucleotide reductase [5], acid phosphatase [6] and oxygen evolving complexes in photosystem II [7].

A few other manganese-containing enzymes i.e., manganese dioxygenase, manganese lipoxygenase (MnLO) [8] and oxalate oxidase [9] with one manganese as an active center are also known. Among these, the most extensively studied enzyme is MnSOD. It catalyzes the dismutation of the superoxide ion and protects living cells against dioxygen dependent toxicities of various organic compounds [10]. The crystal structure from *Thermus Thermophilus* [1] shows that it is tetramer and Mn adopts a trigonal-bipyramidal coordination geometry with a N_3O_2 ligand donor set, one histidyl nitrogen occupies the apical position while water is suggested to sit at the opposite site. The carboxylate oxygen from aspartate is bound to the manganese unidentately. The non-ligating oxygen from the aspartate forms a hydrogen bond with an amino acid residue or the peptide backbone, which is important for the activity of the enzyme (Fig. 1a).

Germin is a manganese-containing enzyme with oxalate oxidase and superoxide dismutase activities [9]. As shown in Fig. 1b, the manganese(II) ion is in an octahedral geometry comprising three histidine, a glutamate and two water

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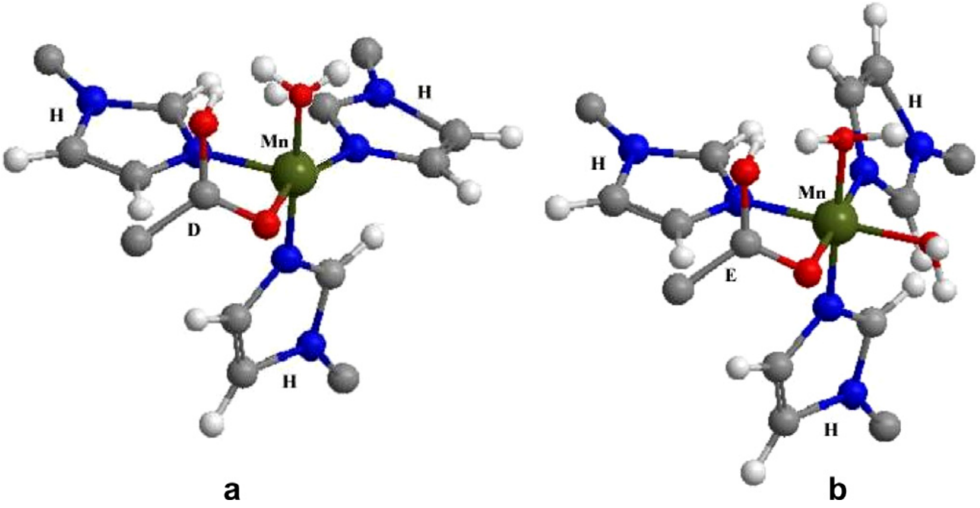


Fig. 1. Active site structure for Mn–SOD (a) and Mn(II)oxlate-oxidase (b).

molecules. The active site structures for other mononuclear manganese enzymes are not known with certainty, but based on their analogous iron enzymes, a square-pyramidal arrangement of two histidines, a glutamate and two water molecules has been proposed for Mn(II)dioxygenase [11] and an active site structure similar to the iron-containing soybean lipoxygenase has been proposed for the manganese lipoxygenase enzyme [12]. According to Minor et al. [13], the iron in iron-lipoxygenase, is coordinated to three nitrogens of histidine residues, one oxygen of a monodentate isoleucine and one oxygen of a weakly coordinated asparagine. A water molecule forming a hydrogen bond with the non-coordinated carboxylate oxygen of isoleucine, completes the distorted octahedral coordination sphere. A common structural feature found in most of the above proteins and enzymes is the presence of one or more carboxylate derived from aspartate/glutamate/isoleucine or asparagine side chains of the protein. These carboxylates act as a bridge between metal ions present in the binuclear manganese containing enzyme and also are suggested to play an important role for structural holding and proton transfer via hydrogen-bonding interactions in proteins [14]. The role of hydrogen bonding in the stabilization of structures as well as in the functions of various metalloproteins is well known in biochemistry [15].

There are several examples of mononuclear and binuclear manganese carboxylate complexes where the hydrogen atoms of the ligand alcohol groups, the bridging aqua or the lattice water molecules form inter/intramolecular hydrogen bonds with coordinated carboxylate groups available in the literature [16], but manganese carboxylate complexes with hydrogen bonds involving pyrazole groups are limited in number. In light of the importance of hydrogen bonded carboxylate and the limited examples of manganese carboxylate complexes with hydrogen bonded pyrazole, we have undertaken the synthesis, structural and SOD activity studies of some manganese carboxylate complexes in the present paper.

2. Experimental

2.1. Materials

All manipulations were carried out under nitrogen atmosphere using standard Schlenk tube techniques unless otherwise stated. The required organic solvents were carefully purified and distilled under nitrogen prior to use, by the literature method [17]. $MnCl_2 \cdot 4H_2O$ (reagent grade) was purchased from E. Merck. Other reagents were of the highest grade commercially available and were used without further purification. 3,5-i-Pr_2pzH [$Pz^{iPr2}H$] (**1**), KHB(3,5-i-Pr_2pz)$_3$ [Tp^{iPr2}] (**2**), [18] KHB(3-Ph,5-Mepz)$_3$ [$Tp^{Ph,Me}$] (**3**) [19] and Tp^{iPr2}MnCl (**4**) [20] were synthesized by the literature methods.

2.2. Physical methods

IR spectra were obtained on a Thermo Nikolet Nexus FT-IR spectrometer in KBr and FD-MS spectra were obtained on a Hitachi M-80 mass spectrometer. Room temperature magnetic susceptibility measurements were done on a Cahn Faraday magnetic susceptibility balance. The X-ray data collection and processing for **5** and **6** were performed on a Rigaku RAXIS-IV imaging plate area detector with Mo Kα radiation ($\lambda = 0.71070$ Å). In the reduction of data, Lorentz and polarization corrections, and empirical absorptions were made [21]. The structure analysis was performed on an IRIS O2 (Silicon Graphics) using the teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan [22]. Neutral scattering factors were obtained from the standard source [23]. The structures were solved by a combination of direct methods (SHELXS-86) [24] and Fourier synthesis (DIRDIF 94) [25]. Least-squares refinements were carried out using SHELXS-97 [24] linked to teXsan. All non-hydrogen atoms were refined anisotropically. Diffraction data for complex **7** were recorded at −80 °C with a Bruker

Smart CCD diffractometer. Emperical absorption corrections were applied. The structure was solved by Patterson methods and refined anisotropically with the SHELX program suite. Hydrogen atoms involved in hydrogen bonding were obtained by refinement, not by fixing the position. Single crystal diffraction studies for **8** and **10** were carried out on a Bruker Smart CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) in a sealed tube at 25 °C. Crystal structures were solved by direct methods and in anisotropic approximation refined using the SHELX TL package [26,27]. Hydrogen atoms were constrained by the rigid model.

2.3. Synthesis of complexes

2.3.1. $[(Pz^{iPr2}H)_4Mn(NO_2\text{–}OBz)_2]$ (5)

(0.197 g, 1.00 mmol) $MnCl_2 \cdot 4H_2O$ and (0.604 g, 4.00 mmol) $Pz^{iPr2}H$ were stirred in 25 mL CH_2Cl_2 and 5 mL CH_3OH for 1 h. To this solution was added a 5 mL acetonitrile solution of sodium *p*-nitrobenzoate (0.378 g, 2.00 mmol) and the reaction mixture was stirred for 12 h at room temperature. The mixture was filtered over celite and the solvent was evaporated to dryness. The compound was dissolved in 5 mL CH_3CN and colorless crystals were obtained at −20 °C (yield 84%). *Anal.* Calc. (%) for $C_{50}H_{72}N_{10}O_8Mn$: C, 60.26; H, 7.28; N, 14.06. Found: C, 60.09; H, 7.31; N, 13.72%. IR (KBr, cm^{-1}), ν(NH of pyrazole) 3211, ν_{as}(COO) 1576, ν_s(COO) 1473, $\mu_{eff} = 5.75$ BM at 295 K.

2.3.2. $[(Pz^{iPr2}H)_4Mn(F\text{–}OBz)_2]$ (6)

(0.197 g, 1.00 mmol) $MnCl_2 \cdot 4H_2O$ and (0.604 g, 4.00 mmol) $Pz^{iPr2}H$ were stirred in 30 mL CH_2Cl_2 and 5 mL CH_3OH for 1 h. A 5 mL acetonitrile solution of sodium *p*-fluorobenzoate (0.324 g, 2.00 mmol) was added to this solution and stirred for 12 h. The mixture was filtered over celite and the solvent was evaporated to dryness. The compound was dissolved in 5 mL acetonitrile and colorless crystals were obtained by slow cooling at −20 °C (Yield 80%). *Anal.* Calc. (%) for $C_{50}H_{72}N_8O_4F_2Mn$: C, 63.72; H, 7.70; N, 11.89. Found: C, 63.49; H, 7.67; N, 11.44%. IR (KBr, cm^{-1}) ν (NH of pyrazole) 3297, ν_{as}(COO) 1570, ν_s(COO) 1442, $\mu_{eff} = 5.78$ BM at 295 K.

2.3.3. $[Tp^{Ph,Me}Mn(OAc)Pz^{Ph,Me}H]$ (7)

$KTp^{Ph,Me}$ (0.521 g, 1.00 mmol) was stirred with $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1.00 mmol) and 1.0 equivalent of $Pz^{Ph,Me}H$ (0.158 g, 1.00 mmol) in 25 mL dichloromethane and 5 mL methanol for 2 h. The mixture was filtered through celite and the filtrate was dried under vacuum. The colorless powder was dissolved in a mixture of dichloromethane and acetonitrile (1:1 ratio) and crystals were obtained by cooling the solution at −20 °C (Yield 65%). *Anal.* Calc. (%) for $C_{42}H_{41}BMnN_8O_2$: C, 66.76; H, 5.47; N, 14.83. Found: C, 66.56; H, 5.39; N, 14.90%. IR (KBr, cm^{-1}), ν(BH) 2539, ν_{as}(COO) 1572, ν_s(COO) 1435, $\mu_{eff} = 5.68$ BM at 295 K.

2.3.4. $[Tp^{iPr2}Mn(Cl)Pz^{iPr2}H]$ (8)

$MnCl_2 \cdot 4H_2O$ (0.197 g, 1.00 mmol), KTp^{iPr2} (0.504 g, 1.00 mmol) and $Pz^{iPr2}H$ (0.761 g, 5.00 mmol) were stirred in 25 mL CH_2Cl_2 and 5 mL CH_3OH for 1 h. The mixture was filtered over celite and the solvent was evaporated to dryness under vacuum. The compound was dissolved in 5.0 mL pentane and 3.0 mL ether. Colorless crystals were obtained from the filtrate at −20 °C in 85% yield. *Anal.* Calc. for $C_{36}H_{62}N_8BClMn$: C, 61.05; H, 8.82; N, 15.82; Cl, 5.00. Found: C, 61.12; H, 8.83; N, 15.97; Cl, 4.80%. IR (KBr, cm^{-1}) ν(BH) 2548, ν(NH of pyrazole) 3292, ν(CN of pyrazole) 1560, $\mu_{eff} = 5.70$ BM at 295 K.

2.3.5. $[Tp^{iPr2}Mn(F\text{–}OBz)]$ (9)

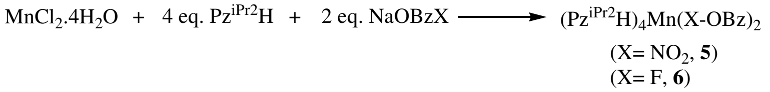
To a 30 mL toluene solution of **4** (0.489 g, 0.882 mmol), was added a 10 mL acetonitrile solution of sodium *p*-fluorobenzoate (0.143 g, 0.882 mmol) and the reaction mixture was stirred for 16 h. The mixture was filtered over celite and the solvent was evaporated under vacuum. A colorless microcrystalline solid was obtained by slow cooling of an acetonitrile solution at −20 °C in 45% yield. *Anal.* Calc. (%) for $C_{34}H_{51}N_6BFO_2Mn$: C, 61.82; H, 7.78; N, 12.27. Found: C, 61.65; H, 7.90; N, 12.07%. IR (KBr, cm^{-1}), ν(BH) 2541, ν_{as}(COO) 1600, ν_s(COO) 1469, $\mu_{eff} = 5.83$ BM at 295 K, FD–MS (m/z) = 660.

2.3.6. $[Tp^{iPr2}Mn_2(\mu\text{-}FOBz)_3(Pz^{iPr2}H)_2]$ (10)

$MnCl_2 \cdot 4H_2O$ (0.168 g, 0.855 mmol), complex **4** (0.474 g, 0.855 mmol), sodium *p*-fluorobenzoate (0.419 g, 2.57 mmol) and $Pz^{iPr2}H$ (0.260 g, 1.71 mmol) in a mixture of toluene and acetonitrile (1:1) were stirred for 12 h at room temperature. The mixture was filtered over celite and the solvent was evaporated to dryness. Colorless crystals were obtained by slow cooling of acetonitrile solution at −20 °C in 65% yield. *Anal.* Calc. (%) $C_{66}H_{90}N_{10}BF_3O_6Mn_2$; C, 61.11; H, 6.99; N, 10.79. Found: C, 60.85; H, 6.95; N, 10.85%. IR(KBr, cm^{-1}), ν(BH) 2538, ν_{as}(COO) 1594, ν_s(COO) 1469, $\mu_{eff} = 5.90/Mn^{2+}$ BM at 295 K.

3. Results and discussion

The reaction of $MnCl_2 \cdot 4H_2O$ with four equivalents of pyrazole **1** and two equivalent of sodium *p*-nitrobenzoate/sodium *p*-fluorobenzoate gave six coordinated mononuclear



$$MnCl_2.4H_2O \; + \; 4\text{ eq. } Pz^{iPr2}H \; + \; 2\text{ eq. NaOBzX} \longrightarrow \underset{\substack{(X= NO_2,\ \mathbf{5})\\(X= F,\ \mathbf{6})}}{(Pz^{iPr2}H)_4Mn(X\text{-}OBz)_2}$$

Scheme 1.

manganese high spin complexes **5** {$C_{50}H_{72}N_{10}O_8Mn$} and **6** {$C_{50}H_{72}N_8O_4F_2Mn$} (Scheme 1). Selected bond distances and bond angles are listed in Table 1 and crystallographic data in Table 2. The Thermal ellipsoid view of the crystal structures for complexes **5** and **6** are given in Figs. 2 and 3, whereas the structure showing intramolecular hydrogen bonding and CH_3–π interactions for these complexes are given in Figs. 4 and 5, respectively. The coordination environment and geometry in complexes **5** and **6** are very similar. As shown in the X-ray structures, both complexes are six coordinated with a distorted octahedral geometry. The manganese–nitrogen and manganese–oxygen bond distances (Table 1) for **5** and **6** are nearly the same. The Mn–N bond distances are slightly longer than the Mn–N bond distances in Mn–Tp^{iPr2} complexes [28]. Also the Mn–O bond distances of coordinated *p*-nitrobenzoate/*p*-fluorobenzoate are slightly longer than the reported manganese carboxylate complexes having the Tp^{ipr2} ligand [28]. In both these complexes, the pyrazole as well as the benzoate groups are behaving as monodentate ligands; the *p*-nitrobenzoate/*p*-fluorobenzoate are coordinated to manganese by only one oxygen atom. The uncoordinated oxygen atom of each benzoate group forms intramolecular hydrogen bonds with two N–H hydrogen atoms attached to the pyrazole rings of $Pz^{iPr2}H$. The different values of the N–O bond distances (O2–N12, 2.833 (3); O2–N22 is 2.873(3) Å in **5** and O2–N12, 2.803 (2); O2–N22 is 2.831(3) Å in **6**), clearly indicate that the hydrogen bonding is stronger in complex **6** than in complex **5**. Besides the existence of intramolecular hydrogen bonding, both of these complexes exhibit a CH_3–π interaction between the CH_3 group of $Pz^{iPr2}H$ and the benzene ring of *p*-nitrobenzoate/*p*-fluorobenzoate as can be judged from the distances between the hydrogen and the centroid of the ring, 3.022 Å in **5** and 3.217 Å in **6** (Figs. 4 and 5). The presence of CH_3–π as well as the π–π stacking interaction is not uncommon in metal complexes [16h]. Several manganese benzoate complexes having Tp ligands have been reported [28], but mononuclear six coordinated manganese carboxylate complexes with intramolecular hydrogen bonding are not very common, except for some octahedral manganese (II) carboxylate complexes [29]. The presence of intramolecular hydrogen bonding as well as a CH_3–π interaction may be responsible for the stability of these complexes, as both are stable under air in the solid as well as in solution state, and they do not react with O_2 or CO_2.

When $Mn(OAc)_2 \cdot 4H_2O$ was allowed to react with $Tp^{Ph,Me}$ in the presence of pyrazole ($Pz^{Ph,Me}H$) (Scheme 2), a five coordinated intramolecular hydrogen bonded manganese (II) complex **7** {$C_{42}H_{41}BMnN_8O_2$} was isolated. As shown in Fig. 6 (Thermal ellipsoid view), the manganese is coordinated with three nitrogen of the $Tp^{Ph,Me}$ ligand. The Mn–N bond distances in complex **7** (Table 1) are very similar to the Mn–N bond distances present in the mononuclear benzoate complex of manganese with Tp^{iPr2} (Mn1–N1, 2.195(4) Å; Mn1–N2, 2.277(4) Å; Mn1–N3, 2.161(3) Å) [28b] but longer than the Fe–N bond distances

Table 1

Selected bond lengths (Å) and angles (°) for [$(Pz^{iPr2}H)_4Mn(NO_2–OBz)_2$] (**5**), [$(Pz^{iPr2}H)_4Mn(F–OBz)_2$] (**6**), [$Tp^{Ph,Me}Mn(OAc)Pz^{Ph,Me}H$] (**7**), [$Tp^{iPr2}Mn(Cl)Pz^{iPr2}H$] (**8**) and [$Tp^{iPr2}Mn_2(\mu\text{-}FOBz)_3(Pz^{iPr2}H)_2$] · CH_3CN (**10** · CH_3CN)

[$(Pz^{iPr2}H)_4Mn(NO_2–OBz)_2$]			
Bond lengths (Å)			
Mn1–N11	2.327(1)	Mn1–N21	2.312(2)
Mn1–O1	2.174(2)	O1–C1	1.268(3)
O2–C1	1.249(3)		
Bond angles (°)			
O1–Mn1–O1	180.00(1)	O1–Mn1–N11	87.84(6)
O1–Mn1–N11	92.16(6)	O1–Mn1–N21	89.25(7)
O1–Mn1–N21	90.75(7)	N11–Mn–N11	180.00(0)
N21–Mn1–N21	180.00(0)		
[$(Pz^{iPr2}H)_4Mn(F–OBz)_2$]			
Bond lengths (Å)			
Mn1–N11	2.329(2)	Mn1–N21	2.327(2)
Mn1–O1	2.175(1)	O1–C1	1.251(2)
O2–C1	1.263(3)		
Bond angles (°)			
O1–Mn1–O1	180.00(0)	O1–Mn1–N11	90.92(6)
O1–Mn1–N11	89.08(6)	O1–Mn1–N21	90.68(6)
O1–Mn1–N21	89.32(6)	N11–Mn–N11	180.00(0)
N21–Mn1–N21	180.00(0)		
[$Tp^{Ph,Me}Mn(OAc)Pz^{Ph,Me}H$]			
Bond lengths (Å)			
Mn1–O1	2.024 (16)	Mn1–N4	2.149(18)
Mn1–N6	2.199(18)	Mn1–N7	2.233(18)
Mn1–N2	2.282(17)		
Bond angles (°)			
O1–Mn1–N4	118.91(7)	O1–Mn1–N6	146.99(7)
N4–Mn1–N6	93.36(7)	O1–Mn1–N7	95.65(7)
N4–Mn1–N7	94.20(7)	N6–Mn1–N7	88.18(6)
O1–Mn1–N2	93.25(7)	N4–Mn1–N2	84.81(6)
N6–Mn1–N2	82.27(6)	N7–Mn1–N2	170.32(6)
[$Tp^{iPr2}Mn(Cl)Pz^{iPr2}H$]			
Bond lengths (Å)			
Mn1–N3	2.151 (19)	Mn1–N5	2.164(2)
Mn1–N1	2.243(19)	Mn1–N7	2.306(2)
Mn1–Cl1	2.419(8)		
Bond angles (°)			
N3–Mn1–N5	95.61(7)	N3–Mn1–N1	82.08(7)
N5–Mn1–N1	80.64(7)	N3–Mn1–N7	90.56(7)
N5–Mn1–N7	89.16(7)	N3–Mn1–Cl1	125.15(5)
N5–Mn1–Cl1	139.15(5)	N1–Mn1–Cl1	105.37(5)
N7–Mn1–Cl1	87.89(5)	N5–Mn1–Cl1	89.16(7)
N2–N1–Mn1	114.89(13)		
[$Tp^{iPr2}Mn_2(\mu\text{-}FOBz)_3(Pz^{iPr2}H)_2$] · CH_3CN			
Bond lengths (Å)			
Mn1–O2	2.133(3)	Mn1–O4	2.193(3)
Mn1–N3	2.238(3)	Mn1–N5	2.240(3)
Mn1–O6	2.255(3)	Mn1–N1	2.293(3)
Mn2–O3	2.096(3)	Mn2–O1	2.107(3)
Mn2–N7	2.216(3)	Mn2–O5	2.271(3)
Mn2–N9	2.272(3)		
Bond angles (°)			
O2–Mn1–O4	88.80(7)	O2–Mn1–O6	91.69(7)
O4–Mn1–O6	93.10(7)	N3–Mn1–O6	169.71(8)
N5–Mn1–O6	87.31(8)	O2–Mn1–N1	94.40(8)

(*continued on next page*)

Table 1 (*continued*)

$[Tp^{iPr2}Mn_2(\mu\text{-}FOBz)_3(Pz^{iPr2}H)_2] \cdot CH_3CN$			
Bond angles (°)			
O4–Mn1–N1	174.02(8)	O3–Mn2–N7	91.82(9)
O1–Mn2–N7	88.63(9)	N7–Mn2–O5	113.94(8)
O3–Mn2–N9	96.62(8)	O5–Mn2–N9	81.00(7)
O1–Mn2–N9	171.62(8)	N7–Mn2–N9	88.06(9)
O5–Mn2–N9	81.00(7)		

(Fe1–N1, 2.2626(15) Å; Fe1–N2, 2.0745(15) Å; Fe1–N3, 2.0855(16) Å) in a mononuclear iron acetate complex with Tp^{Ph2} [30]. The Mn–N bond distance of the coordinated $Pz^{Ph,Me}H$ (Mn1–N7, 2.234 (18) Å) is similar to the Fe–N bond distance with 3,5-diphenylpyrazole (Fe1–N4, 2.2347 (17) Å), but shorter than the Mn–N bond distance with $Pz^{iPr2}H$ coordination (Mn1–N4, 2.304 (4) Å). The acetate behaves as a monodendate ligand in **7** where one oxygen atom is bonded with the manganese center and the other oxygen atom forms a hydrogen bond with the proton lying on the nitrogen of $Pz^{PhMe}H$ coordinated at the apical position to the manganese ion. The carboxylate oxygen from asparate in Mn–SOD is also bound to the manganese unidentately as is the acetate anion in complex **7**. The existence of a hydrogen bond in complex **7** is clearly established on the basis of the location of the hydrogen bond with mean bond distances of Ha–O2, 1.909 Å and Ha–N8, 0.859 Å. The presence of a hydrogen bond also affects the appearance of the *ν*(NH) band in the IR spectrum of the complex as the free $Pz^{PhMe}H$ gives the band at 3180 cm^{-1}. The short distance of the carbonyl oxygen (O_2) of the acetate anion from the nitrogen of neutral pyr-

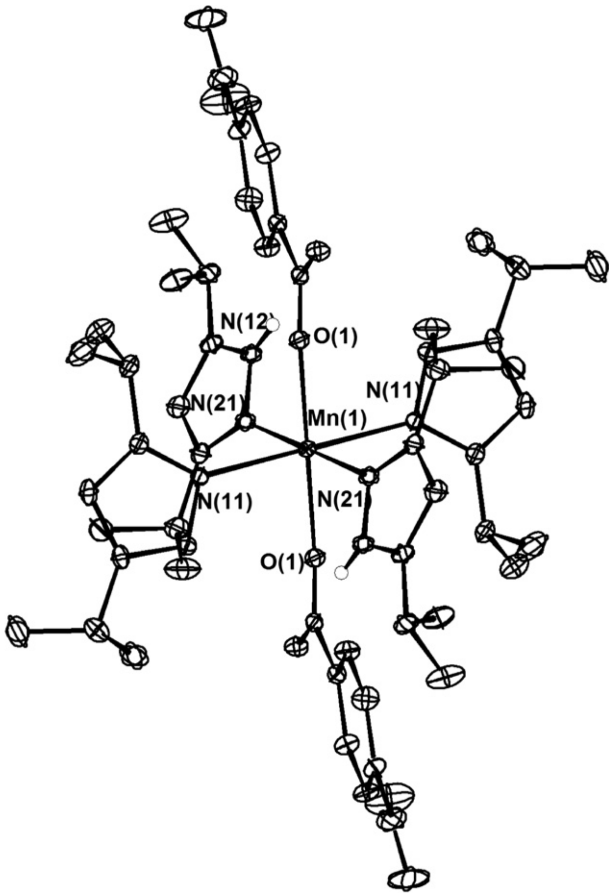


Fig. 2. Thermal ellipsoid view of complex **5** drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

Table 2
Crystallographic data for $[(Pz^{iPr2}H)_4Mn(NO_2\text{–}OBz)_2]$ (**5**), $[(Pz^{iPr2}H)_4Mn(F\text{–}OBz)_2]$ (**6**), $[Tp^{Ph,Me}Mn(OAc)\ Pz^{Ph,Me}H]$ (**7**), $[Tp^{iPr2}Mn(Cl)Pz^{iPr2}H]$ (**8**) and $[Tp^{iPr2}Mn_2(\mu\text{-}FOBz)_3(Pz^{iPr2}H)_2] \cdot CH_3CN$ (**10** · CH_3CN)

	5	**6**	**7**	**8**	**10** · CH_3CN
Empirical formula	$C_{50}H_{72}N_{10}O_8Mn$	$C_{50}H_{72}N_8O_4F_2Mn$	$C_{42}H_{41}BMnN_8O_2$	$C_{36}H_{62}BClMnN_8$	$C_{68}H_{90}BF_3Mn_2N_{11}O_6$
Formula weight	996.12	942.10	755.58	708.14	1335.20
Crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$ (no. 2)
Lattice parameters					
a (Å)	10.715(6)	10.948(2)	11.7003(19)	13.312(2)	12.3069(16)
b (Å)	11.344(4)	12.663(3)	11.7630(19)	16.941(3)	13.4695(18)
c (Å)	12.747(8)	18.695(3)	15.425(3)	17.528(3)	24.205(3)
α (°)	100.33(3)	90.00(0)	86.927(3)	90.00(0)	81.3(0)
β (°)	107.16(2)	96.035(9)	87.581(3)	92.428(3)	80.22(0)
γ (°)	105.97(3)	90.00(0)	64.696(2)	90.00(0)	64.15(0)
V ($Å^3$)	1364(1)	2577.5(9)	1916.1(5)	3949.5(12)	3544.87(80)
Z	1	2	2	4	2
D_{calc} (g/cm^3)	1.212	1.214	1.310	1.191	1.251
Data collection					
μ(Mo Kα) (cm^{-1})	0.300	0.313	0.392	0.437	0.420
θ_{max} (°)	27.4	27.5	28.79	28.28	28.02
Number of measured reflections	5582	5613	17275	7344	26591
Number of observed reflections	4752	4352	6410	6922	10845
Number of parameters refined	329	311	491	442	841
R	0.0625	0.0588	0.0442	0.0514	0.0579
R_w	0.1756	0.1664	0.1313	0.1335	0.1591

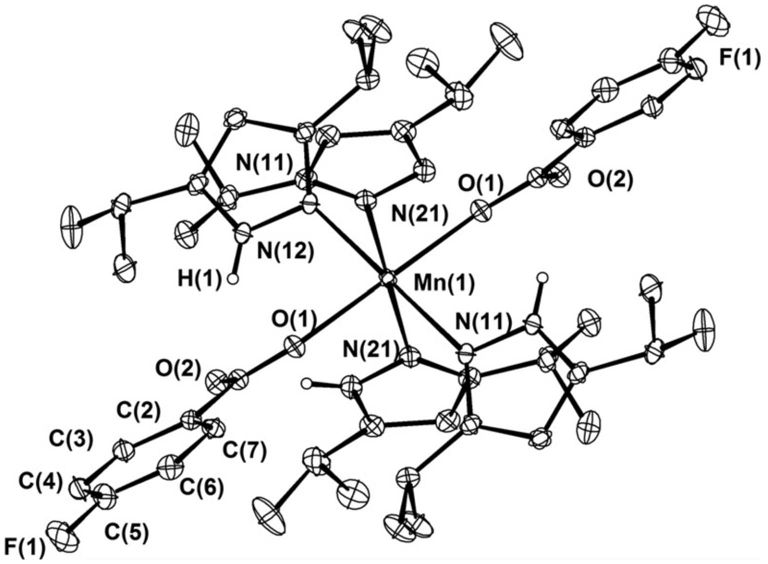


Fig. 3. Thermal ellipsoid view of complex **6** drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

azole (N8) (O2–N8 bond, 2.76 Å), also suggest the presence of hydrogen bonding in **7**.

The Mn–O bond distance (Mn1–O1, 2.0240 (16) Å) is very similar to the Mn–O bond distance in a mononuclear hydrogen bonded manganese benzoate complex (Mn1–O1, 2.043(4) Å) [28b] but larger than the Fe–O1 bond distance in a mononuclear hydrogen bonded iron acetato complex (Fe–O1, 1.9634 (14) Å) [30]. The geometry of this complex is trigonal bipyramidal with one nitrogen (N2) from $\mathrm{Tp}^{\mathrm{PhMe}}$ and N7 of the neutral pyrazole in apical positions.

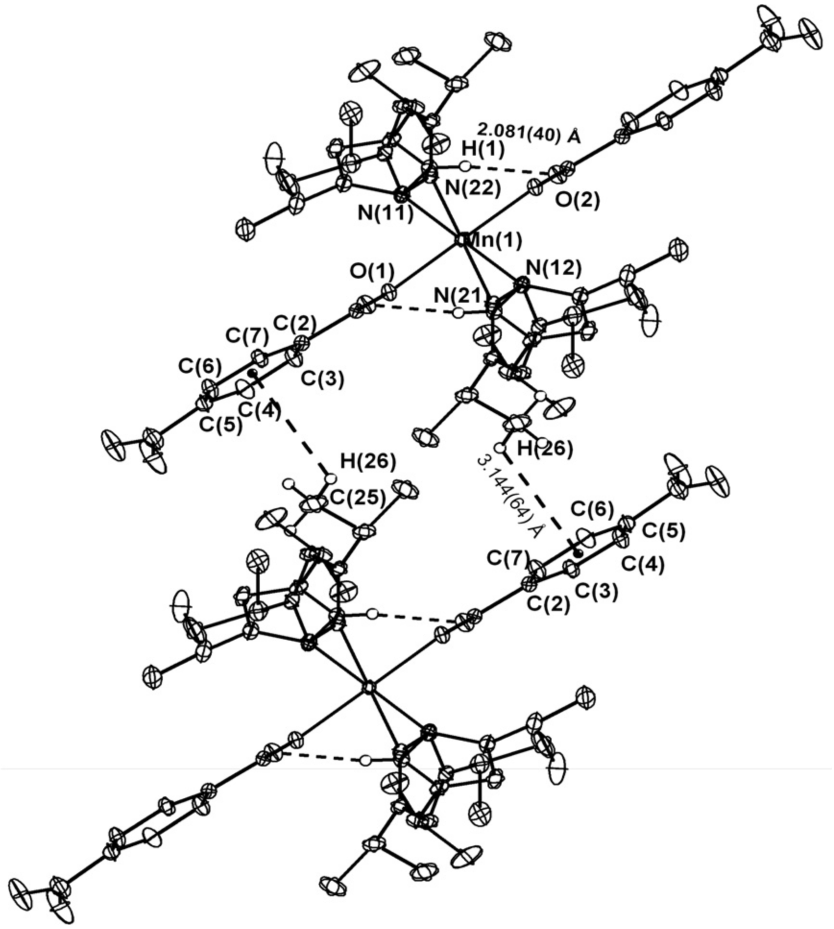


Fig. 4. Molecular structure showing intramolecular hydrogen bonding and CH_3–π interactions in complex **5**.

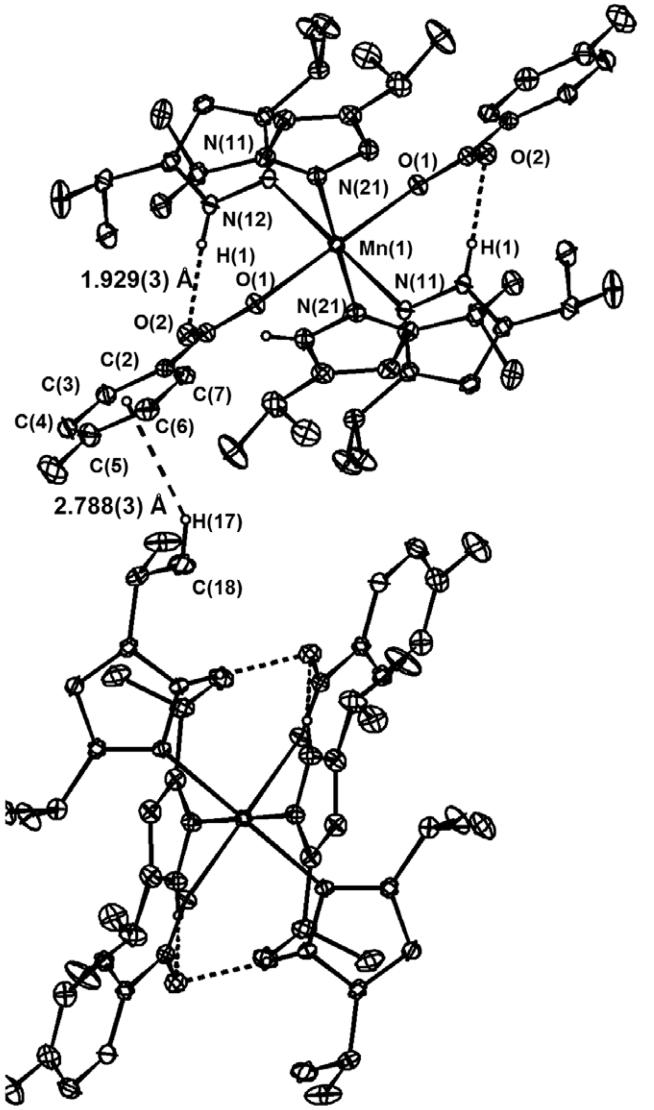


Fig. 5. Molecular structure showing intramolecular hydrogen bonding and CH_3–π interactions in complex **6**.

In another set of experiments, we have prepared $\mathrm{Tp}^{i\mathrm{Pr}2}\mathrm{MnClPz}^{i\mathrm{Pr}2}\mathrm{H}$, $\{C_{36}H_{62}N_8BClMn\}$ (**8**) as a starting material for the preparation of other various manganese complexes. Complex **8** was prepared by the reaction of $MnCl_2 \cdot 4H_2O$ with $\mathrm{KTp}^{i\mathrm{Pr}2}$ in the presence of 1.5 equivalents of $\mathrm{Pz}^{i\mathrm{Pr}2}\mathrm{H}$, as shown in Scheme 3. Complex **8** is a mononuclear high spin manganese (II) species. As shown in the crystal structure (Fig. 7), it is five coordinate having a N_4Cl ligand donor set with a distorted geometry. The Mn1–Cl1 bond distance is 2.4193 Å, which is longer than the Mn–Cl bond distance in $Mn_2Cl_4(O{-}C_6H_4{-}p\text{-}CH_3)_2^{-2}$ (2.32 Å) [31] and [MnTPPCl](K222)] (2.364 Å) [31c], but similar to the Mn–Cl terminal bond distance in LMn_2Cl_2Br (2.411 Å) [31b]. The distances between manganese and nitrogens of the coordinated $\mathrm{Tp}^{i\mathrm{Pr}2}$ slightly differ from each other (Mn1–N1, 2.2425 (19) Å; Mn1–N3, 2.1507 Å; Mn1–N5, 2.164 (2) Å) and are considerably longer than the distances reported for $[Mn(HB(3,5\text{-}Mepz)_3)]^{+2}$ (1.96–1.98 Å) [32] and 2.05–2.23 Å in $[Mn_2O(O_2(CH_3)_2)(HB(pz)_3)_2] \cdot CH_3CN$ [33].

Using the literature method [20] we have prepared the complex $\mathrm{Tp}^{i\mathrm{Pr}2}\mathrm{MnCl}$, $\{C_{34}H_{51}N_6BFO_2Mn\}$ (**4**) by reacting $MnCl_2 \cdot 4H_2O$ and $\mathrm{KTp}^{i\mathrm{Pr}2}$ in a 1:1 ratio, to act as a starting material for the synthesis of complexes **9** $\{C_{34}H_{51}N_6BFO_2Mn\}$ and **10** $\{C_{66}H_{90}N_{10}BF_3O_6Mn_2\}$. Complex **9** was prepared by the reaction of **4** with one equivalent of sodium *p*-fluorobenzoate (Scheme 4). The spectroscopic characterization revealed that the benzoate group coordinates in a bidentate fashion. Although the crystal structure of **9** could not be determined, based on other spectroscopic data and the X-ray structure of a five coordinate cobalt fluorobenzoate complex with $\mathrm{Tp}^{i\mathrm{Pr}2}$ [34], we infer that **9** is also a monomeric five coordinate Mn(II) complex.

We have also succeeded in synthesizing an unsymmetrical fluorobenzoate bridged binuclear manganese (II) complex. The reaction of **4** with **1**, $MnCl_2 \cdot 4H_2O$ and sodium

$$Mn(OAc)_2.4H_2O \;+\; \mathrm{KTp}^{\mathrm{Ph,Me}} \;+\; \mathrm{Pz}^{\mathrm{Ph,Me}}\mathrm{H} \longrightarrow \mathrm{Tp}^{\mathrm{Ph,Me}}\mathrm{Mn(OAc)Pz}^{\mathrm{Ph,Me}}\mathrm{H}$$

7

Scheme 2.

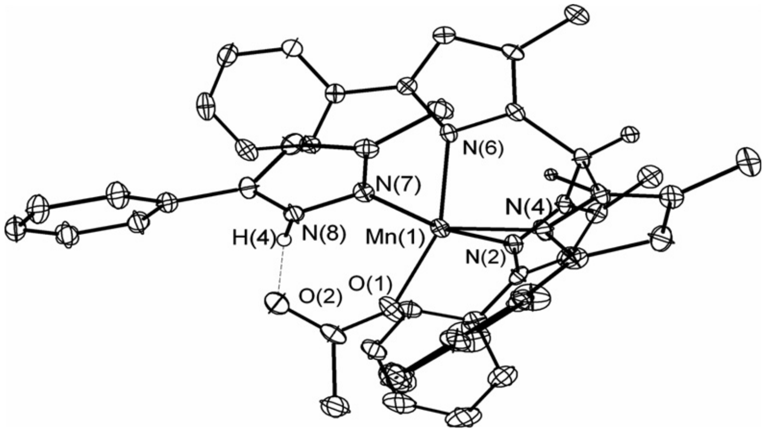


Fig. 6. Thermal ellipsoid view of complex **7**. All hydrogen atoms have been omitted for clarity.

$$\mathrm{MnCl_2.4H_2O} + \mathrm{KTp^{iPr2}} + \mathrm{Pz^{iPr2}H} \longrightarrow \underset{\mathbf{8}}{\mathrm{Tp^{iPr2}Mn(Cl)Pz^{iPr2}H}}$$

Scheme 3.

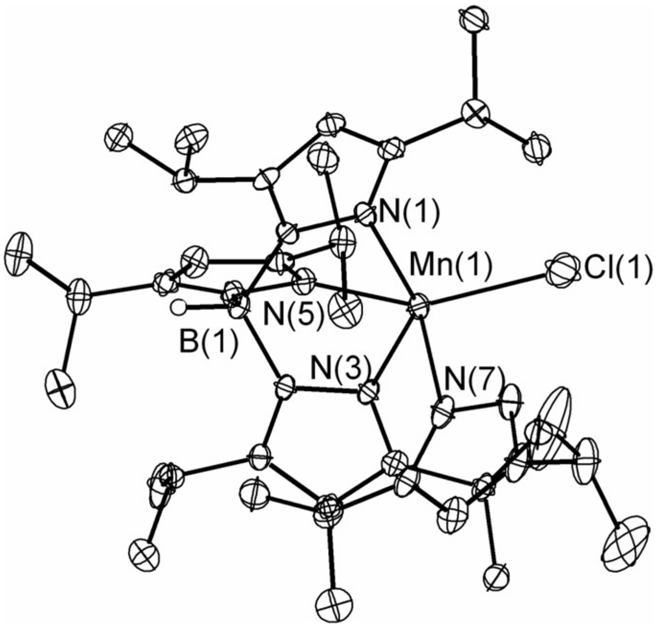
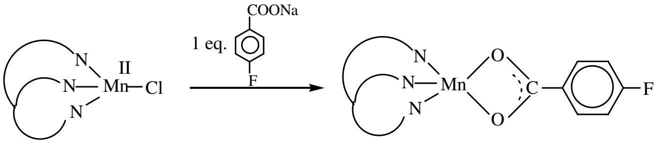


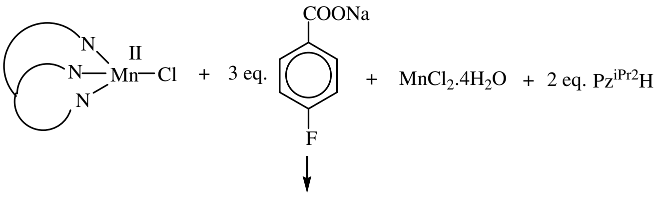
Fig. 7. Thermal ellipsoid view of complex **8** drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.



9

Scheme 4.

p-fluorobenzoate in mixed solvent (toluene:acetonitrile in a 1:1 ratio) gave complex **10** (Scheme 5). The presence of an IR band at 3297 $\mathrm{cm^{-1}}$ (due to the νN–H stretching band) in the IR spectrum of this complex suggested the existence of pyrazole in the protonated form. The molecular structure of **10** was determined by X-ray crystallography and its Thermal ellipsoid view is given in Fig. 8. As shown in Fig. 8, both manganese (II) ions are in the same environment. The two manganese (II) ions are bridged with three fluorobenzoate groups in an unsymmetrical manner with a Mn–Mn separation of 3.732(4) Å. Like the previously reported benzoate bridged binuclear manganese complex by Osawa et al. [35], in complex **10** both manganese ions are also in an octahedral environment and two of the μ-fluorobenzoate groups are symmetrically bridging, whereas the third one adopts a unique coordination mode i.e., only one oxygen from the carboxylate serves as a bridging ligand, while the other one binds to Mn2 terminally. A structurally similar (μ-carboxylato)$_3$ unit has been reported in a linear trinuclear manganese(II) carboxylato complex [36]. The Mn–Mn separation found in complex **10** is 3.732(4) Å, which is close to 3.739(2) Å [37] and 3.612(2) Å [38] in (μ-aqua)(bis(μ-carboxylato)dimanganese(II)) complexes but shorter than 4.034(2) Å in a symmetrical tris(μ-carboxylato)$_3$ complex [39]. The short metal–metal distance in **10** reflects the unusual nature of the tris(μ-fluorobenzoato)$_3$ unit with one oxygen atom from a fluorobenzoate group acting as a bridging ligand. The magnetic susceptibility of the powdered sample is 8.34 BM per mol. Efforts were also made for the successful removal of one bridging fluorobenzoate without disturbing the manganese bimetallic core, but the reaction of **10** with one equivalent of NaOH in toluene resulted in the formation of a mononuclear manganese (II) fluorobenzoate complex similar to **9**, in contrast to the pyrazole adduct as reported by Osawa et al. [35]. The resultant complex is five coordinated with a $\mathrm{N_3O_2}$ ligand donor set and the fluorobenzoate group is coordinated to the manganese bidentately.



$\mathrm{Tp^{iPr2}Mn_2(\mu\text{-}FOBz)_3(Pz^{iPr2}H)_2}$

10

Scheme 5.

3.1. Superoxide dismutase activity studies

The complexes **5**–**8** and **10** were tested for their SOD activity using xanthine–xanthine oxidase–nitro blue tetrazolium (NBT) methods [40], as the coordination number around manganese in these complexes is close to the coordination number around the manganese in manganese-containing SOD enzyme [1] and also they have intramolecular hydrogen bonding, except in complexes **8** and **10**. The test was performed separately in duplicate for each compound in 3 ml of 50 mM potassium phosphate buffer (pH 7.4) at 25 °C in the absence of EDTA. The reaction mixture was prepared as follows:

Fifty micromoles of NBT, 50 μM xanthine, 1000 U/ml catalase and 0.04 U/ml xanthine oxidase were used to produce superoxide ions in solution. The formation of diformazan was monitored at 560 nm wavelength. The $\mathrm{IC_{50}}$ value in Fig. 9 means the concentration of the complex which exerts SOD activity equivalent to one unit of native SOD. Out of these tested complexes only complex **7** exhibited $\mathrm{IC_{50}}$ values

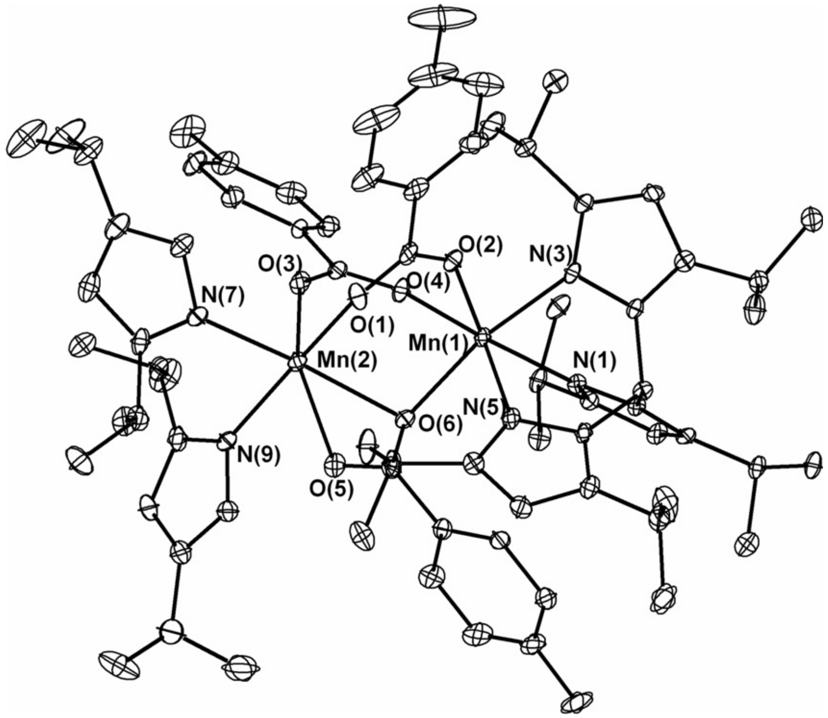


Fig. 8. Thermal ellipsoid view of complex **10** drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

at 3.5 μM concentration (Fig. 9), clearly indicating that this may be a suitable model for a SOD mimic. The SOD activity value for **7** is much better than the previously reported SOD model complexes screened by the NBT method under the same conditions [41], but lower than the SOD model complex reported by Kitajima et al. [28b]. Also the ability of complex **7** to disproportionate O_2^- is comparatively better than the most active systems based on salen or porphyrin ligands reported by several workers [42]. The better SOD activities of complex **7** may be attributable to the very close structural similarities of this complex with the active site of native Mn–SOD.

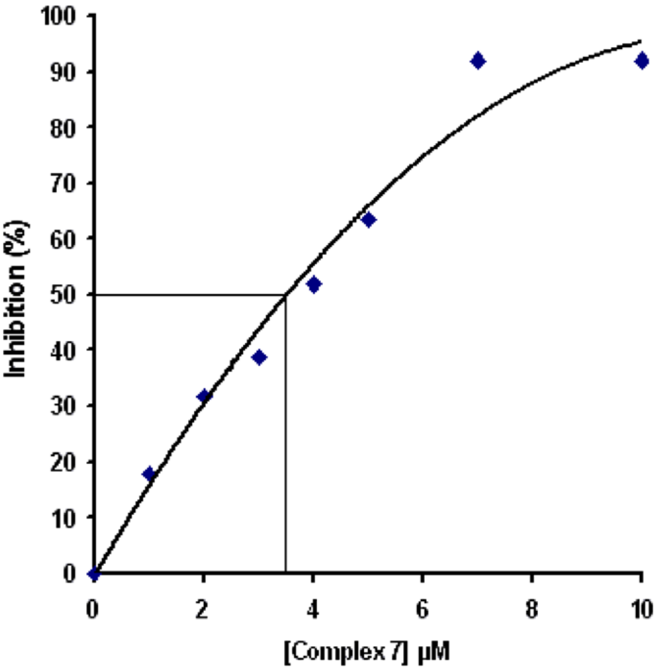


Fig. 9. SOD activity of complex **7** in xanthene oxidase-NBT assay.

4. Conclusion

We have reported several manganese carboxylate complexes, both with hydrogen as well as non-hydrogen binding, having five and six coordination numbers. The results presented in this paper demonstrated that different coordination modes of the carboxylate groups are possible simply by changing the supporting nitrogen donor ligands. It is possible to get the hydrogen bonded carboxylate complexes simply by adding the corresponding pyrazole to the reaction mixture as demonstrated in the formation of complex **7**, or by using pyrazole as a supporting ligand in the reaction as shown by the preparation of complexes **5** and **6**. The reaction of $Pz^{iPr2}H$ with $MnCl_2 \cdot 4H_2O$ and sodium *p*-nitrobenzoate/sodium *p*-fluorbenzoate resulted in the formation of octahedral complexes with intramolecular hydrogen bonding and CH_3–π interactions. The SOD activity studies on complexes **5**–**8** and **10** suggested that complex **7** seems to be a good model mimic of the native Mn–SOD enzyme as complex **7** has a suitable active site structure as well as intermolecular hydrogen bonding.

5. Supporting data

The crystallographic data have been deposited with the CCDC. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on requesting, quoting the deposition numbers CCDC 293641–293644 and CCDC 293653, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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