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Manganese complexes as models for manganese-containing pseudocatalase enzymes: Synthesis, structural and catalytic activity studies

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Abstract

Manganese complexes of the type [TpMn(X)] and [TpMn(μ-N_3)(μ-X)MnTp] (X = acetylacetonate, acac; picolinate, pic and Tp = $Tp^{Ph,Me}$ for acac, Tp = Tp^{ipr2} for pic complexes) having $Tp^{Ph,Me}$ (hydrotris(3-phenyl,5-methyl-pyrazol-1-yl)borate)/Tp^{ipr2} (hydrotris(3,5-diisopropyl-pyrazol-1-yl)borate) as a supporting ligand have been synthesized and structurally characterized. IR and X-ray structures suggest that complexes **7** and **9** are binuclear with azido and bidentate ligands (acac/pic) bridging, whereas complexes **6** and **8** are mononuclear with a 5-coordinated metal center. In complex **9** the picolinate is coordinated as tridentate in a η_3-fashion, but in complex **7** acac behaves as bidentate, whereas azide is coordinated in a bridging bidentate μ-1,3-manner in both **7** and **9**. Since the coordination geometry of the manganese ions in complex **9** is very similar to the active site structure of manganese-containing pseudocatalase, we have tested the catalytic activity of the same towards the disproportionation of hydrogen peroxide. The catalytic results indicated that complex **9** has reasonably good catalase activity and may be suitable, structurally as well as functionally, as a model for the pseudocatalase enzyme.

Keywords: Pyrazolylborate; Carboxylate; Azide; Manganese; Pseudocatalase; Crystal structure

1. Introduction

Catalase enzymes are present in most aerobic forms of life and are responsible for the decomposition of hydrogen peroxide to molecular oxygen and water [1]. Although, most catalases contain the iron-protoporphyrin IX prosthetic group, some bacteria utilize a non-heme, Mn-containing catalase. Many Mn catalases have been identified [2,3] but those from *Thermus thermophilus* and *Lactobacillus plantarum* have been best studied. Some microorganisms, which are unable to synthesized heme can nevertheless produce a catalase. This catalase, which in contrast to heme-containing catalase, is not inhibited by CN^- or N_3^-, and is called pseudocatalase/azide insensitive. On the basis of various model complexes of manganese reported in the literature, it has been concluded that the active site structure of both catalase as well as pseudocatalase is basically the same, however their working mechanism may be different.

The recently reported crystal structure of Mn-containing catalase from *L. plantarum* [4] demonstrated that it has hexameric units. Each subunit contains a dimanganese active site. The manganese ions are linked by a μ-1,3-bridging glutamate carboxylate and two single atom solvent bridges (oxo, hydroxo or aquo) that electronically couple the centre. In addition, each manganese ion is coordinated by one histidine nitrogen and one carboxylate. For the Mn1 subsite, the carboxylate (Glu35) is monodentate, with the non-coordinated oxygen forming a six atom hydrogen-bonded loop including the solvent bridge, indicating that the bridge is protonated in the resting state. The sixth

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(apical) position of this subsite is occupied by a third non-bridging solvent molecule coordinated to the dimanganese cluster. Terminally bound water molecules are easily displaced from the metal complexes and this apical site likely serves as the initial substrate binding site during catalysis. The other subsite (Mn2) has a bidentate (chelating) coordination mode for glutamate, which may prevent exogenous ligands from binding and makes each of the manganese ions six-coordinate in the cluster, with approximately octahedral geometry at each subsite. The Mn–Mn separation in the resting state of the enzyme is 3.03 Å and both manganese centres are in the three oxidation state. The EXAFS analysis of the same protein predicted a Mn–Mn separation of 3.53 Å in the fully reduced state, i.e. 2,2 oxidation state [5]. It is well known that the azide ion acts as an inhibitor of *L. plantarum* catalase forming an active site complex. The crystal structure of the azide coordinated protein is virtually indistinguishable from the native structure except in the vicinity of the active site, where significant differences occur. In the azide complex of the oxidized form of the enzyme, the anion occupies a terminal position on the Mn1 subsite, replacing the solvent present in the native structure. Since azide is an analog of hydrogen peroxide, this mode of bonding is likely to mimic that of the coordinated substrate. The X-ray structure of azide bonded catalase in the oxidized state revealed the terminal bonding mode for the coordinated azide, however the coordination mode of azide in the reduced state of the enzyme is not definitely known.

Carboxylato bridged dinuclear Mn complexes have attracted much attention in recent years because of their potential biological relevance [6] in different manganese containing enzymes [7]. While several dinuclear Mn complexes having (μ-oxo)bis(μ-carboxylato) [8], (μ-hydroxo)-bis(μ-carboxylato) [9], (μ-hydroxo)(μ-acetato) [10], (μ-hydroxo)bis(μ-acetato) [11] bridges are known, no example exist of dinuclear manganese complexes with a (μ-azido)(μ-carboxylato) bridging unit. As a part of our synthetic effort towards modelling the active site of Mn-containing protein by using the hindered tris(pyrazolyl)borate as a supporting ligand, we now report on dinuclear complexes bridged with a single carboxylato and a single azido unit along with other carboxylate complexes of manganese (II), and their catalytic activity.

2. Experimental

2.1. Materials

All solvents used were purified by the literature methods [12]. Reagents of the highest grade commercially available were used without further purification. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk tube techniques unless otherwise stated. 3,5-iPr_2pzH [$Pz^{iPr2}H$] (**1**), KHB(3,5-$iPr_2pz)_3$ [Tp^{iPr2}] (**2**) [13], KHB(3-Ph,5-Mepz)$_3$ [$Tp^{Ph,Me}$] (**3**) [14] and Tp^{iPr2}MnCl (**4**) [15] were synthesized by the literature methods.

2.2. Physical methods

IR spectra were obtained on a Thermo Nikolet Nexus FT-IR spectrometer in KBr discs. Room temperature magnetic susceptibility measurements were done on a Princeton applied research vibrating sample magnetometer Model 155 whereas the magnetic susceptibility measurements at variable temperature (from liquid helium to room temperature) were performed on a Quantum Design Squid Magnetometer Model MPMS. The X-ray data collection and processing for **6** and **9** were performed on a Kappa Apex Bruker CCD detector with Mo Kα radiation ($\lambda = 0.71070$ Å). In the reduction of data, Lorentz and polarization corrections, and empirical absorption corrections were made. All non-hydrogen atoms were refined aniostropically. The structures were solved by Patterson methods and refined anisotropically with the SHELX program suite [16]. Hydrogen atoms were constrained by a rigid model.

2.3. Synthesis of the complexes

2.3.1. [$Tp^{Ph,Me}$MnCl] (**5**)

$MnCl_2 \cdot 4H_2O$ (0.198 g, 1.0 mmol) was stirred with **3** (0.521 g, 1.0 mmol) in 10 mL CH_3OH and 20 mL CH_2Cl_2 for 1 h. The solution was filtered over celite and the solvent was evaporated to dryness under vacuum. Crystallization of complex **5** from acetonitrile yielded a colorless solid in 89% (0.51 g, 0.89 mmol.) yield. *Anal.* Calc. for $C_{30}H_{28}N_6BClMn$: C, 62.79; H, 4.91; N, 14.64; Cl, 6.17. Found: C, 63.00; H, 4.82; N, 14.36; Cl, 6.21%. IR (KBr, cm^{-1}): ν(BH) 2541.

2.3.2. [$Tp^{Ph,Me}$Mn(acac)] (**6**)

To an acetonitrile (30 mL) solution of complex **5**, one equivalent of sodium acetylacetonate (0.109 g, 0.89 mmol) was added and the resulting solution was stirred for 8 h. The reaction mixture was filtered over celite and the solvent was evaporated to dryness under vacuum. Crystals suitable for X-ray data collection were obtained by slow cooling of the compound in a mixture of CH_2Cl_2 and CH_3CN in 75% (0.43 g, 0.67 mmol.) yield. *Anal.* Calc. for $C_{35}H_{36}N_6O_2BMn$: C, 65.84; H, 5.68; N, 13.16. Found: C, 66.00; H, 5.82; N 13.06%. IR (KBr, cm^{-1}): ν(BH) 2539, ν(CO) 1594. Magnetic moment μ_{eff} (295 K) = 5.78 BM.

2.3.3. [$Tp^{Ph,Me}$Mn(μ-N_3) (μ-acac)Mn $Tp^{Ph,Me}$] (**7**)

The reaction of complex **6** (0.427 g, 0.67 mmol) in dichloromethane (20 mL) and sodium azide (0.043 g, 0.67 mmol) in methanol (10 mL) for 3 h followed by filtration over celite and evaporation to dryness under vacuum resulted in the formation of compound **7** in 77% (0.35 g, 0.52 mmol) yield. *Anal.* Calc. for $C_{65}H_{64}N_{15}O_2B_2Mn_2$: C, 64.05; H, 5.29; N, 17.23. Found: C, 63.90; H, 5.22; N, 17.16%. IR (KBr, cm^{-1}): ν(BH) 2514, ν(CO) 1596, $\nu(N_3)$ 2075. Magnetic moment μ_{eff} (295 K) = 5.57 BM/Mn^{2+}.

*2.3.4. [Tp^{ipr2}Mn(pic)] (**8**)*

To a dichloromethane (20 mL) solution of **4** (0.556 g, 1.0 mmol) was added a 10 mL methanolic solution of potassium picolinate (0.161 g, 1.0 mmol), and the resulting solution was stirred for 3 h. After this time, the reaction mixture was filtered over celite. The evaporation of solvent under vacuum resulted in a white crystalline compound in 64% (0.41 g, 0.64 mmol) yield. *Anal.* Calc. for $C_{33}H_{50}N_7O_2BMn$: C, 61.68; H, 7.84; N, 15.23. Found: C, 61.59; H, 7.94; N, 15.43%. IR (KBr, cm^{-1}), ν(BH) 2538, ν_{as}(COO) 1592, ν_s(COO) 1470. Magnetic moment μ_{eff} (295 K) = 5.83 BM.

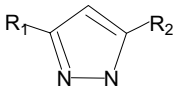
*2.3.5. [Tp^{ipr2}Mn(μ-N$_3$)(μ-pic)Mn(Pz^{ipr2})Tp^{ipr2}] (**9**)*

The reaction of complex **8** (0.411 g, 0.64 mmol), Pz^{ipr2}H (0.097 g, 0.64 mmol) and sodium azide (0.041 g, 0.64 mmol) in 20 mL dichloromethane and 10 mL methanol for 3 h resulted in the formation of complex **9**. The resulting solution was filtered over celite and evaporated to dryness under vacuum. The solid was dissolved in a mixture of dichloromethane and acetonitrile (1:1 ratio) and a crystalline compound was obtained by slow cooling of the solution at 4 °C in 36% (0.310 g, 0.23 mmol) yield. *Anal.* Calc. $C_{69}H_{112}N_{18}O_2B_2Mn_2$: C, 61.06; H, 8.32; N, 18.57. Found: C, 61.39; H, 8.56; N 18.69%. IR (KBr, cm^{-1}), ν(BH) 2545, ν_{as}(COO) 1593, ν_s(COO) 1469, ν(N$_3$) 2077. Magnetic moment μ_{eff} (295 K) = 5.68 BM/Mn^{2+}.

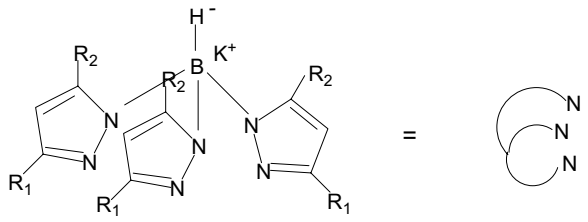
3. Results and discussion

As reported in our previous work [17], the reaction of a binuclear Mn(II) di(μ-hydroxo) complex with one equivalent of benzoic acid results in the replacement of one hydroxide ligand to give the corresponding bimetallic (μ-hydroxo)(μ-benzoato) complex. Further replacement of the bridging hydroxide with azide gave a binuclear Mn(II) complex [18]. Due to the high solubility of this compound in the majority of organic solvents, we could not get a suitable single crystal for X-ray structure determination. However on the basis of IR and other spectroscopic techniques, a (μ-azido)(μ-benzoato) bridged manganese (II) dimer complex was proposed.

In our effort to prepare a model compound for Mn-containing pseudocatalase, first we prepared the starting complexes Tp^{iPr2}MnCl (**4**) and Tp^{Ph,Me}MnCl (**5**). The starting materials were prepared by reacting manganese (II) chloride with both 3-phenyl,5-methyl and 3,5-diisopropyl-substituted pyrazolylborate ligands (Fig. 1). The starting materials viz., **4** and **5** (Fig. 2) when treated with sodium acetylacetonate/sodium picolinate gave 5-coordinated manganese (II) complexes Tp^{Ph,Me}Mn(acac) (**6**) and Tp^{iPr2}Mn(pic) (**8**) (Fig. 3). The IR data suggested that both acac and pic are coordinated in a bidentate manner. The single crystal X-ray study of **6** suggested that the manganese ion is coordinated by three nitrogen atoms of Tp^{Ph,Me} and two oxygen atoms of acetylacetonate (Fig. 4). The Mn–N bond distances range from 2.178(2) to 2.230(2) Å



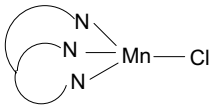
R$_1$, R$_2$ = (CH$_3$)$_2$CH- 1



R$_1$, R$_2$ = (CH$_3$)$_2$CH- 2

R$_1$ = CH$_3$ R$_2$ = C$_6$H$_5$- 3

Fig. 1. Chemdraw structures of **1**, **2** and **3**.



R$_1$, R$_2$ = (CH$_3$)$_2$CH- 4

R$_1$ = CH$_3$ R$_2$ = C$_6$H$_5$- 5

Fig. 2. Chemdraw structures of **4** and **5**.

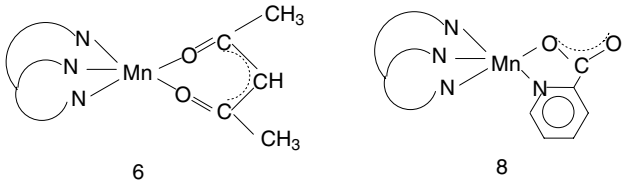


Fig. 3. Chemdraw structures of **6** and **8**.

and fall in the range of reported Mn–N bond distances of manganese complexes having other Tp ligands [19]. The Mn–O bond distances of the coordinated acetylacetonate, Mn(1)–O(1), Mn(1)–O(2), are 2.078(2) Å. These Mn–O bond distances are well within the range of other Mn–O bond distances [20]. The IR band at 1592, (ν_{as}(COO)) and 1470, (ν_s(COO)) cm^{-1} in the picolinate complex suggest the bidentate coordination mode of the ligand. Although, a crystal structure is not available for complex **8**, other data suggest the same structure with a 5-coordinated manganese center as is seen for **6**. Both complexes **6** and **8** were used for the synthesis of the corresponding azido complexes. When complexes **6** and **8** in dichloromethane solvent were treated with a methanolic solution of sodium azide for 3 h, **7** and **9** (Fig. 5) were formed, respectively. Although both these reaction were carried out in the presence of an excess amount of azide, no detectable amount of [TpMn(N$_3$)] was formed. Thus, the formation of **7** and **9** is a thermodynamically favorable reaction. Detailed characterization of these

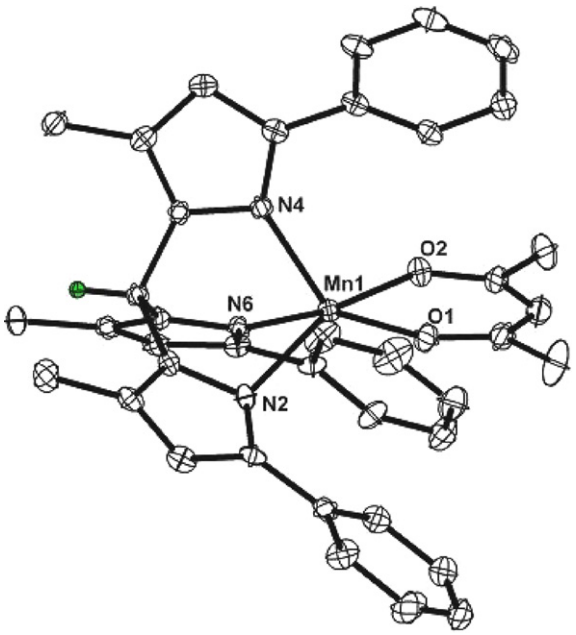
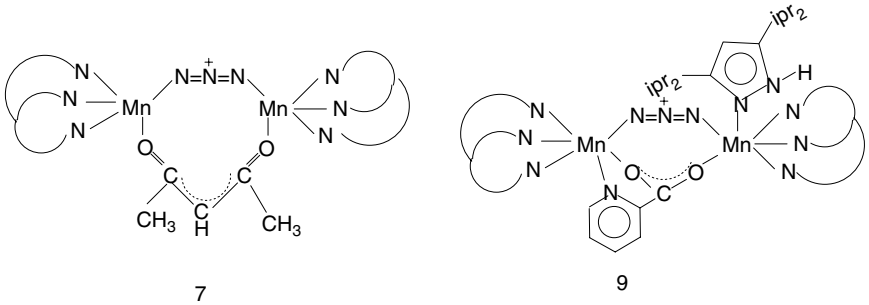


Fig. 4. Thermal ellipsoid view of complex **6** drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

complexes revealed that both complexes have azide coordination where each metal center is 6-coordinated in **9** and 5-coordinated in complex **7**. IR data demonstrated that in both **7** and **9**, the azide ligands are coordinated in a μ-1,3-fashion. Complex **7** could not be crystallized as single crystals, but slow recrystallization of **9** from dichloromethane and acetonitrile at 4 °C gave single crystals suitable for X-ray studies. The X-ray data collection for **9** was performed at 100 K (Table 1) and a thermal ellipsoid view is given in Fig. 6. The molecular structure of **9** (Fig. 6) represents a novel (μ-1,3-azido)(μ-picolinato) bridging core. This is the first example of such a structure, while a (μ-hydroxo)(μ-1,3-azido) binuclear copper complex with Tp^{iPr2} was reported previously [21].

As shown in Fig. 6, each manganese is in a 6-coordination sphere as is present in Mn-containing catalase/pseudocatalase. The most interesting feature of this structure is that the picolinate ligand is behaving as a tridentate ligand in this complex, where one nitrogen and one oxygen is coordinated with one manganese center and only one oxygen is coordinated with the other manganese center in an asymmetric manner. The tridentate coordination nature



7 9

Fig. 5. Chemdraw structures of **7** and **9**.

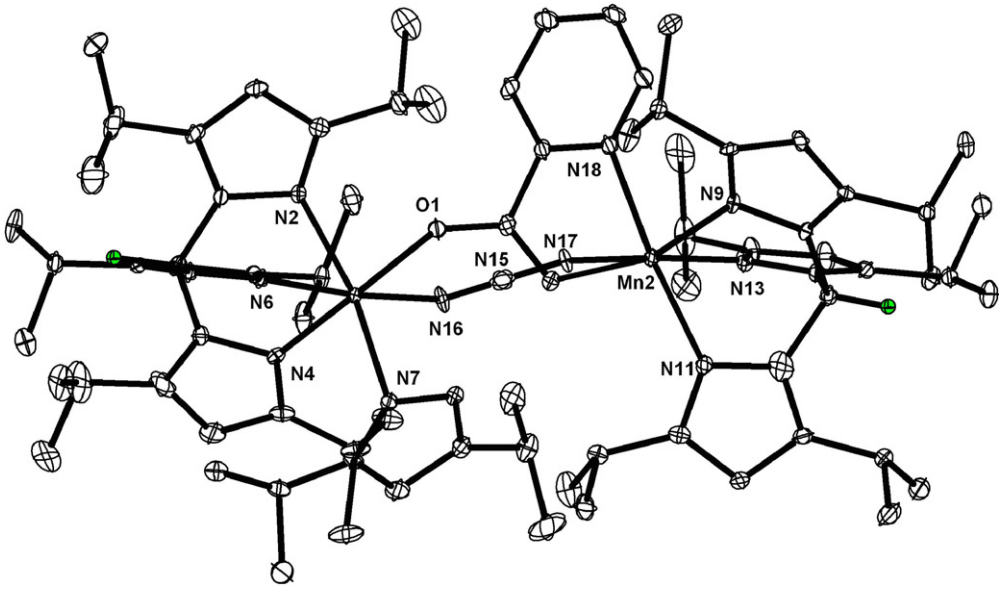


Fig. 6. Thermal ellipsoid view of complex **9** drawn at the 30% probability level. All hydrogen atoms have been omitted for clarity.

Table 1
Crystallographic data for [$Tp^{Ph,Me}$Mn(acac)] (**6**) and [Tp^{ipr2}Mn(μ-N_3)-(μ-pic)Mn(Pz^{ipr2})Tp^{ipr2}] (**9**)

	6	**9**
Formula weight	723.37	1496.44
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P21/n$
Lattice parameters		
a (Å)	11.7457(17)	13.290(2)
b (Å)	11.8283(17)	31.649(5)
c (Å)	15.670(2)	21.206(3)
α (°)	101.839(2)	90.00
β (°)	94.360(2)	106.881(7)
γ (°)	119.440(2)	90.00
V (Å^3)	1815.2(4)	8535(2)
Z	2	4
D_{calc} (g/cm^3)	1.324	1.165
Data collection		
μ (Mo Kα) (cm^{-1})	0.551	0.352
θ_{max} (°)	28.79	25.55
Number of parameters refined	433	978
R	0.0758	0.0542
R_w	0.1966	0.0854

Table 2
Selected bond lengths (Å) and angles (°) for [$Tp^{Ph,Me}$Mn(acac)] (**6**) and [Tp^{ipr2}Mn(μ-N_3)(μ-pic)Mn(Pz^{ipr2}) Tp^{ipr2}] (**9**)

*$Tp^{Ph,Me}$Mn(acac) (**6**)*			
Bond lengths (Å)			
Mn(1)–O(1)	2.078(2)	Mn(1)–O(2)	2.078(2)
Mn(1)–N(2)	2.202(2)	Mn(1)–N(4)	2.178(2)
Mn(1)–N(6)	2.230(2)		
Bond angles (°)			
O(2)–Mn(1)–O(1)	85.16(8)	O(2)–Mn(1)–N(4)	111.93(9)
O(1)–Mn(1)–N(4)	108.30(8)	O(2)–Mn(1)–N(2)	156.95(9)
O(1)–Mn(1)–N(2)	93.25(8)	N(4)–Mn(1)–N(2)	90.44(8)
O(2)–Mn(1)–N(6)	92.12(8)	O(1)–Mn(1)–N(6)	157.69(9)
N(4)–Mn(1)–N(6)	93.29(8)	N(2)–Mn(1)–N(6)	80.67(8)
*Tp^{ipr2}Mn(μ-pic)(μ-N_3)Mn(Pz^{ipr2})Tp^{ipr2} (**9**)*			
Bond lengths (Å)			
Mn(1)–N(2)	2.281(5)	Mn(1)–N(4)	2.231(5)
Mn(1)–N(6)	2.253(5)	Mn(1)–N(7)	2.313(5)
Mn(1)–N(16)	2.183(5)	Mn(1)–O(1)	2.231(4)
Mn(2)–N(9)	2.216(5)	Mn(2)–N(11)	2.208(5)
Mn(2)–N(13)	2.262(5)	Mn(2)–N(17)	2.207(5)
Mn(2)–N(18)	2.297(5)	Mn(2)–O(2)	2.251(4)
Bond angles (°)			
N(16)–Mn(1)–O(1)	85.29(17)	N(16)–Mn(1)–N(4)	90.14(19)
O(1)–Mn(1)–N(4)	174.35(17)	N(16)–Mn(1)–N(6)	173.7(2)
O(1)–Mn(1)–N(6)	93.97(16)	N(4)–Mn(1)–N(6)	90.20(17)
N(16)–Mn(1)–N(2)	92.54(19)	O(1)–Mn(1)–N(2)	95.22(16)
N(4)–Mn(1)–N(2)	81.64(18)	N(6)–Mn(1)–N(2)	81.25(18)
N(16)–Mn(1)–N(7)	97.42(19)	O(1)–Mn(1)–N(7)	89.81(16)
N(4)–Mn(1)–N(7)	94.08(18)	N(6)–Mn(1)–N(7)	88.86(17)
N(2)–Mn(1)–N(7)	169.18(17)	N(11)–Mn(2)–N(17)	95.59(19)
N(11)–Mn(2)–N(9)	87.13(18)	N(17)–Mn(2)–N(9)	91.31(18)
N(11)–Mn(2)–O(2)	108.76(16)	N(17)–Mn(2)–O(2)	81.93(16)
N(9)–Mn(2)–O(2)	163.19(17)	N(11)–Mn(2)–N(13)	80.72(19)
N(17)–Mn(2)–N(13)	175.9(2)	N(9)–Mn(2)–N(13)	86.84(18)
O(2)–Mn(2)–N(13)	100.80(16)	N(11)–Mn(2)–N(18)	171.39(19)
N(17)–Mn(2)–N(18)	93.01(19)	N(9)–Mn(2)–N(18)	93.03(18)
O(2)– Mn(2)–N(18)	72.10(16)	N(13)–Mn(2)–N(18)	90.69(19)

of picolinate is not uncommon and a few examples have been reported earlier [22], but to the best of our knowledge this is the first report of a (μ-azido)(μ-picolinato) binuclear manganese (II) complex where picolinate is showing tridentate behavior. Mn1 is coordinated with three nitrogen atoms of Tp^{iPr2} and one nitrogen of free pyrazole whereas Mn2 is coordinated with only three nitrogen atoms of Tp^{iPr2} ligand. The azide molecule is coordinated with both manganese centres, bridging in a η-1,3-fashion. The striking feature of the tridentate behaviour of picolinate is that in this complex the coordination sphere of both manganese ions are six, as in native catalase/pseudocatalase enzyme, with a slight difference of the coordinating ligands in the vicinity of the metal ions. In the native enzyme it has been reported that the azide ions act as inhibitors and the crystal structure of the azide bonded catalase demonstrated that the binding of azide is terminal where as in complex **9** the azide is bonded in a bridging mode. Binuclear transition metal complexes with (μ-azido)(μ-carboxylato) are very rare in the literature [23]. The coordination mode of the azide ligand in the oxidized state of catalase is well known, but still there is speculation about the binding mode of this ligand in the reduced state. Also it has been reported in the literature that the metal–metal separation in the reduced state of the enzyme is more than that of the oxidized form and there is strong belief that the binding mode of the azide ligand may also change to bridging in the reduced form, which may be responsible for the large separation of the manganese ions. In fact the Mn–Mn separation in binuclear complexes is very much dependent on the presence of bridging ligands as evident from the Mn–Mn separation in different complexes with the Tp^{iPr2} ligand (Table 3). The Mn–Mn separation in di(μ-hydroxo) dimanganese (II) (3.33 Å), changes to 3.603(2) Å in (μ-hydroxo)(μ-pyrazolato) dimanganese(II) [24], 2.706 Å in di(μ-oxo)(μ-acetato) dimanganese (III,IV) [10] and 2.70 Å in di(μ-oxo) dimanganese (III) [15]. This distance further increases when azide is present in the bridging mode. In complex **9**, the Mn–Mn separation is 5.355 Å. The Mn–Mn separation of 5.355 Å in complex **9** gives us strong support to propose that the terminal mode of azide in the oxidized form of pseudocatalase changes to a bridging mode in the reduced form. The Mn–N bond distances of both coordinated Tp^{iPr2} ligands are in the range 2.208–

Table 3
The distances between Mn–Mn ions in different binuclear complexes of the hydrotris(3,5-diisopropyl-pyrazol-1-yl)borate ligand

Complex	Mn1–Mn2 distance (Å)	Reference
$TpMn^{II}(\mu\text{-}OH)_2Mn^{II}Tp$	3.314(1)	[15]
$TpMn^{III}(\mu\text{-}O)_2Mn^{III}Tp$	2.696(2)	[15]
$TpMn^{II}(\mu\text{-}OH)(\mu\text{-}3,5\text{-}Pr^i_2pz)Mn^{II}Tp$	3.603(2)	[24]
$TpMn^{II}(\mu\text{-}OBz)_3Mn^{II}$ $(3,5\text{-}Pr^i_2pz)_2$	3.753(2)	[19]
$TpMn^{III}(\mu\text{-}O)_2(\mu\text{-}OAc)Mn^{IV}Tp$	2.709(1)	[10]
$TpMn^{II}(\mu\text{-}OBz)_3Mn^{II}$ (Tp^iPr_2)	4.006(1)	[17]

2.281 Å, as reported for other complexes of this ligand. The bond distance of coordinated 3,5-diisopropylpyrazole (Mn1–N7, 2.313 Å) is larger than the Mn–N bond distance of Tp^{iPr2} (Table 2). The Mn–N bond distances of the coordinated azide (Mn1–N16, 2.183; Mn1–N17, 2.207 Å) are very similar to the Cu–N bond distance in the azide bridged dinuclear copper complex (Cu–N4, 2.06 Å) [21].

In complex **9**, both manganese centres (Mn1 and Mn2) are also linked to each other by a μ-1,3-OCO bridge, whereas the nitrogen of picolinate is coordinated to Mn2 only, forming a five coordinate ring as shown in Fig. 6. Fig. 7 shows the interaction between two independent molecules and Fig. 8 shows the packing diagram of the compound. As shown in Fig. 7, a CH_3–π interaction appears

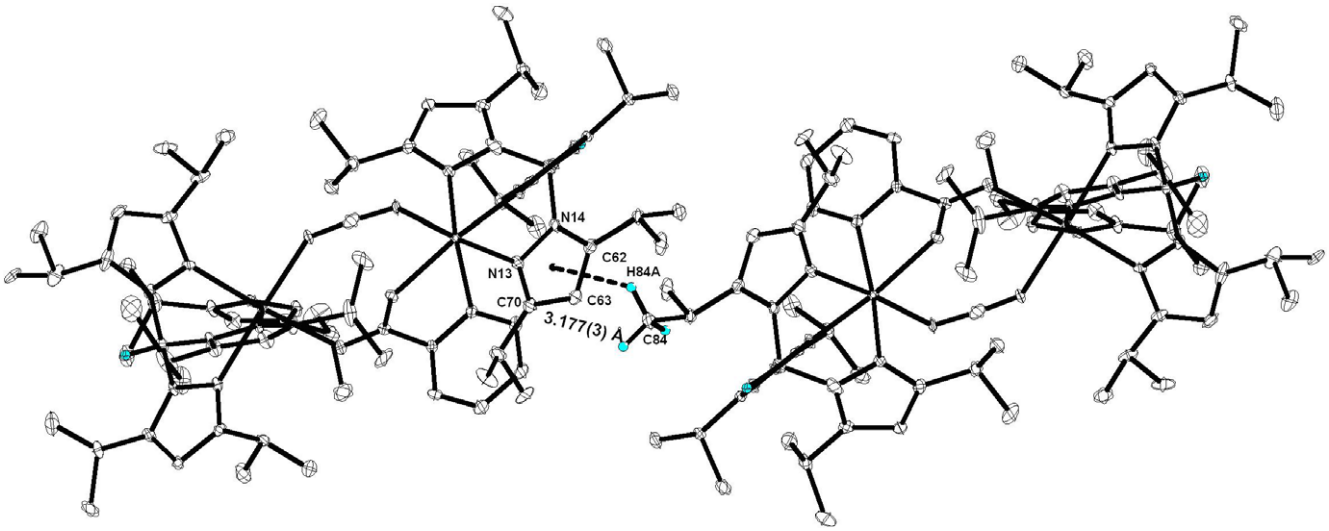


Fig. 7. Molecular structure showing CH_3–π interaction in complex **9**.

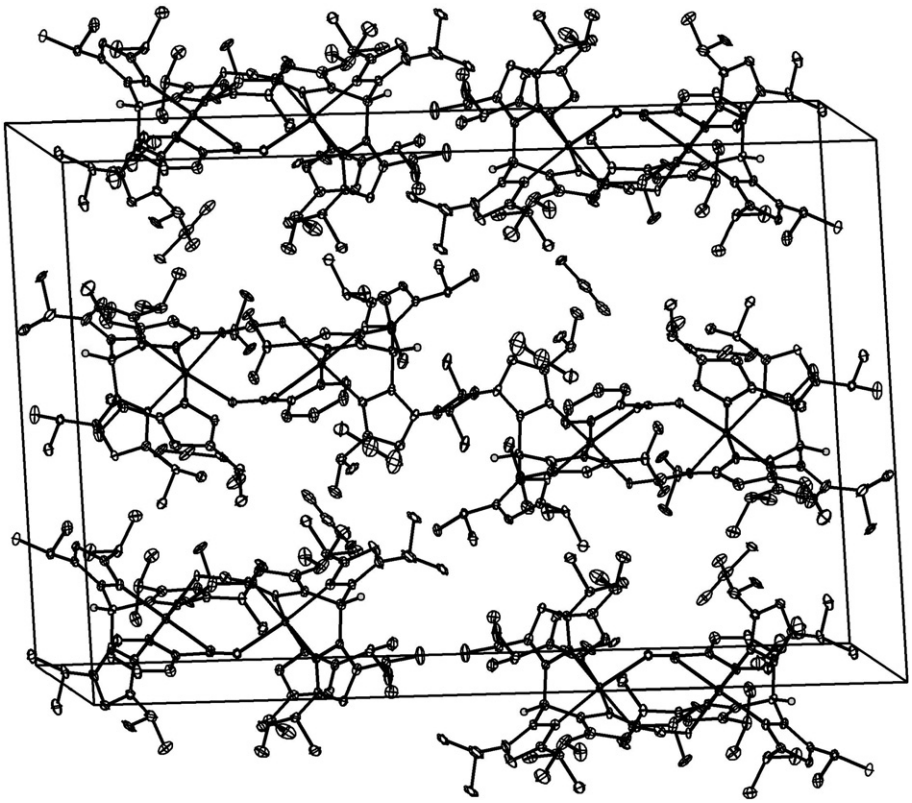


Fig. 8. Packing view of complex **9**.

to exist between the two independent molecules with a separation of 3.177(3) Å.

3.1. Magnetic studies

The room temperature magnetic moment for all the reported complexes are well within the range of magnetic moment reported for manganese (II) complexes [25,26]. Since the coordination structure of complex **9** is very close to the active site structure of manganese containing catalase/pseudocatalase, its magnetic properties has been reported at variable temperatures ranging from helium to room temperature. Fig. 9 shows the temperature dependence plot of μ_{eff} (○) and χ_M (△). The value of μ_{eff} at 300 K amounts to 5.69 μ_B, close to the spin-only value of 5.92 μ_B for $S = 1/2$. The effective magnetic moment smoothly decreases with temperature. The χ_M versus T curve shows maxima at approximately 44 K and then declines rapidly to zero at 6 K, indicating the presence of weak antiferromagnetic coupling between the manganese ions [26].

3.2. Catalytic activity studies

3.2.1. Electronic spectra

Complexes **7** and **9** exhibit no absorption band in the visible region, suggesting that both manganese ions in these complexes are in the two oxidation state. In order to get an insight into the disproportionation of H_2O_2 catalyzed by complexes **7** and **9**, the reaction was monitored by absorption spectroscopy. The UV–vis absorption spectra of these complexes (showing no bands) are very similar to the optical spectrum (lack of visible absorption) of manganese catalase from *T. thermophilus* (TTC) in the reduced (II, II) state [27]. During the reaction of **9** with H_2O_2 in methanol, a new band at 379 nm wavelength appeared and the intensity of this band increases with increasing concentration of hydrogen peroxide until the reaction is completed.

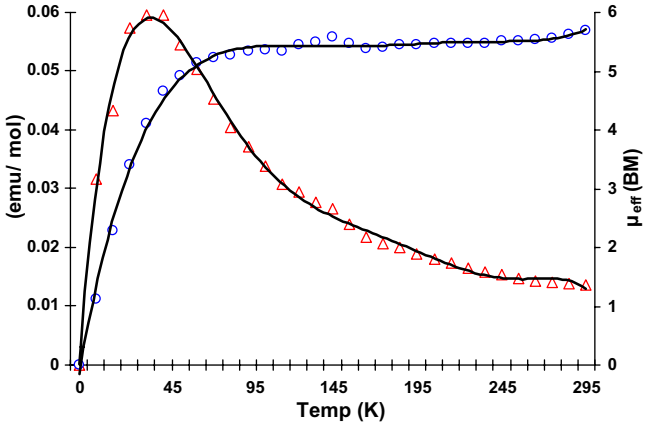


Fig. 9. Plot of μ_{eff} (○) and χ (△) vs. temperature for complex **9**.

3.2.2. Kinetics

Since the coordination geometry of complex **9** is very similar to the active site structure of pseudocatalase, the kinetic experiment of complex **9** with H_2O_2 was performed in detail. An excess concentration of H_2O_2 was used in the reaction to measure the initial rate of oxygen evolution and formation of new manganese species in methanol at room temperature. The order of the reaction with respect to the catalyst was measured by varying the catalyst concentration at a constant concentration of H_2O_2. The initial rate versus catalyst concentration showed a good linear correlation (Fig. 10). The linear dependence of the rate with respect to the catalyst revealed that the reaction is first order. The slope of the line gives a first order rate constant $(k) = 9.725 \times 10^{-4}\ s^{-1}$ for a H_2O_2 concentration of 24.47 mM. The rate constant for complex **9** is slower as compared to other model compounds reported in the literature [28,29]. At a constant concentration, complex **9** exhibits saturation kinetics with H_2O_2 and follows the Michaelis–Menten equation. The catalytic turnover number $(k_{cat}) = 6.676 \times 10^{-3}\ s^{-1}$ and the Michaelis constant (K_M) is 114 mM (Fig. 11). As reported in the literature, some catalases whose activity was not inhibited by CN^- or azide (N_3^-) are called pseudocatalase. The interesting aspect of **9** is that in spite of azide binding, it exhibits catalytic activity and catalyses the disproportionation of hydrogen peroxide.

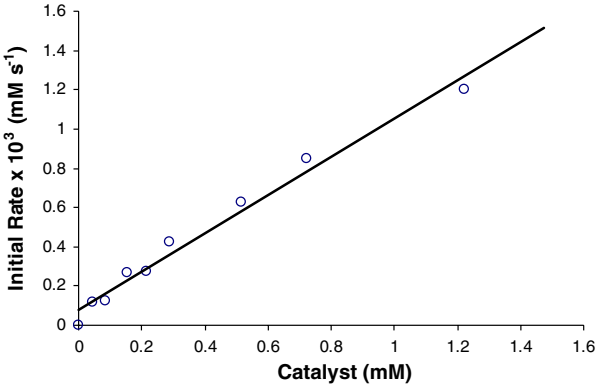


Fig. 10. Effect of the [catalyst] on the initial rate of H_2O_2 disproportionation at 25 °C and $[H_2O_2] = 24.47$ mM in methanol.

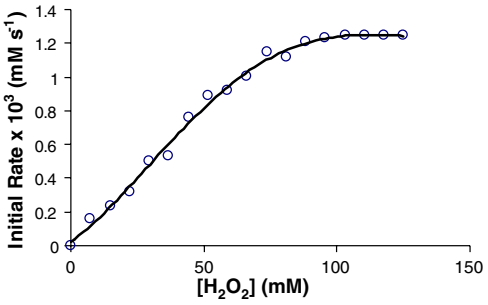


Fig. 11. Effect of the $[H_2O_2]$ on the initial rate of H_2O_2 disproportionation at 25 °C and [catalyst] = 368 μM in methanol.

4. Conclusion

In conclusion, we have reported the synthesis, structural as well as catalytic studies of some manganese compounds as suitable models for manganese-containing pseudocatalase. To the best of our knowledge complex **9** is the first manganese complex that is a μ-1,3-azido bridged dimer having picolinate as a bridging ligand. The most striking feature of this complex is that the picolinate is behaving as tridentate ligand, which is not very common. Due to the tridentate nature of picolinate, each manganese center is 6-coordinated which is very important for the catalytic activity of pseudocatalase. The coordination number of each manganese ion in **7** is five where the acetylacetonate behaves as a bidentate ligand. The interesting observation is that complex **9** has the capability for disproportionation of hydrogen peroxide but complex **7** does not because the coordination geometry of this complex is not very similar to the active site structure of the native enzyme. Thus, complex **9** may be a true model for manganese-containing pseudocatalase both structurally as well as functionally.

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Appendix A. Supplementary material

CCDC 633945 and 633946 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.03.049.

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