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# A mixed-valence diacetate-bridged $Mn^{II}$–$Mn^{III}$ complex incorporating a bridging phenolate ligand

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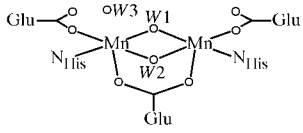
The synthesis and characterization of a new unsymmetrical dinucleating *N*,*O*-donor ligand, 2-[*N*,*N*-bis(2-pyridylmethyl)-aminomethyl]-6-[*N*-(3,5-di-*tert*-butyl-2-oxidobenzyl)-*N*-(2-pyridylamino)aminomethyl]-4-methylphenol ($H_2$Ldtb), as well as the X-ray crystal structure of its corresponding mixed-valence diacetate-bridged manganese complex, di-$\mu$-acetato-$\mu$-{2-[*N*,*N*-bis(2-pyridylmethyl)aminomethyl]-6-[*N*-(3,5-di-*tert*-butyl-2-oxidobenzyl)-*N*-(2-pyridylamino)aminomethyl]-4-methylphenolato}dimanganese(II,III) tetraphenylborate, [$Mn^{II}$-$Mn^{III}$($C_{42}H_{49}N_5O_2$)($C_2H_3O_2$)$_2$]($C_{24}H_{20}B$), are reported. The complex may be regarded as an interesting structural model for the mixed-valence $Mn^{II}$–$Mn^{III}$ state of manganese catalase.

## Comment

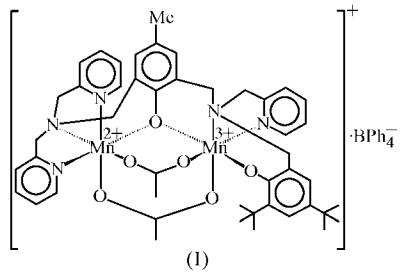
Catalases are enzymes responsible for hydrogen peroxide dismutation, according to the reaction $2H_2O_2 \rightarrow O_2 + 2H_2O$. The dimanganese catalase extracted from *Thermus thermophilus* was recently characterized by X-ray diffraction analysis, which confirmed the existence of a dinuclear manganese centre in the active site situated in a cavity rich in hydrophobic residues (see scheme) (Barynin *et al.*, 1997; Antonyuk *et al.*, 2000). The Mn···Mn distance is 3.18 Å in the reduced form ($Mn_2^{II}$) and 3.14 Å in the oxidized form ($Mn_2^{III}$). On the other hand, the mixed-valence $Mn^{II}$–$Mn^{III}$ oxidation state is the least well characterized, and the *Lactobacillus plantarum* enzyme has not been shown to form a stable $Mn^{II}$–$Mn^{III}$ form (Waldo *et al.*, 1995; Khangulov *et al.*, 1990). In fact, the design of biomimetic systems aiming to help in the understanding of



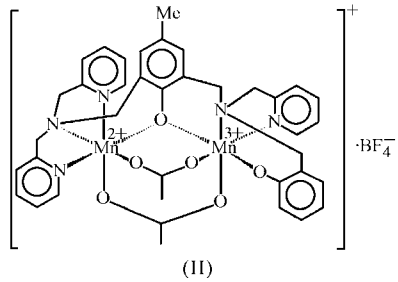

the mechanism of $H_2O_2$ disproportionation by manganese catalases has attracted many research groups (Wu *et al.*, 2004).

We report here the synthesis and X-ray structure of the title novel mixed-valence $Mn^{II}$–$Mn^{III}$ complex, (I), containing the unsymmetrical dinucleating ligand $Ldtb^{2-}$ {$H_2$Ldtb is 2-[*N*,*N*-bis(2-pyridylmethyl)aminomethyl]-6-[*N*-(3,5-di-*tert*-butyl-2-oxidobenzyl)-*N*-(2-pyridylmethylamino)amino]-4-methylphenol} and acetate bridges, as a further interesting structural model for mixed-valence $Mn^{II}$–$Mn^{III}$ catalase.

The asymmetric unit of (I) consists of a discrete [$Mn^{II}$-$Mn^{III}$(Ldtb)($\mu$-OAc)$_2$]$^+$ cation complex and a tetraphenylborate counter-ion. In the crystal structure, the packing arrangement is governed by electrostatic forces between ion pairs. The molecular structure of (I) (Fig. 1) shows that, in the dinuclear [$Mn^{III}Mn^{II}$(Ldtb)($\mu$-OAc)$_2$]$^+$ unit, the $Mn^{III}$ and $Mn^{II}$ ions are bridged by phenolate atom O1 of the $Ldtb^{2-}$ ligand and by two carboxylate groups of the acetate ligands. The charge distribution is the major contributor to the enhanced stability of the mixed-valence species, as observed by Dubois *et al.* (2003). Atoms N1, N22 and N32, from the tertiary amine and two pyridine groups (soft side), complete the octahedral coordination sphere of Mn1, typical of high-spin $Mn^{II}$ (Karsten, Neves, Bortoluzzi, Stähle & Maichle-Mössmer, 2002). A comparison of the bond lengths around the six-coordinated $Mn^{II}$ ion (Table 1; mean 2.201 Å) are in good agreement with those reported by Karsten, Neves, Bortoluzzi, Strähle & Maichle-Mössmer (2002) for the compound [$Mn^{II}$-$Mn^{III}$(bpbpmp)(OAc)$_2$]$BF_4$, (II), where $H_2$bpbpmp is the ligand {2-[*N*,*N*-bis(2-pyridylmethyl)aminomethyl]-6-[(2-hydroxybenzyl)(2-pyridylmethyl)]aminomethyl}-4-methylphenol, and by Karsten, Neves, Bortoluzzi, Lanznaster & Drago, (2002) in the compound [$Mn^{II}Fe^{III}$(bpbpmp)(OAc)$_2$]($ClO_4$), (III).




(I)




(II)

The distances around $Mn^{II}$ average 2.210 Å in (II) and 2.206 Å in (III), with the same $N_3O_3$ environment as (I). The distances from the pyridine N atom to Mn1 in (I) are quite similar [2.237 (3) and 2.262 (4) Å], while the distance of the N atom *trans* to the oxygen bridge is slightly longer, reflecting

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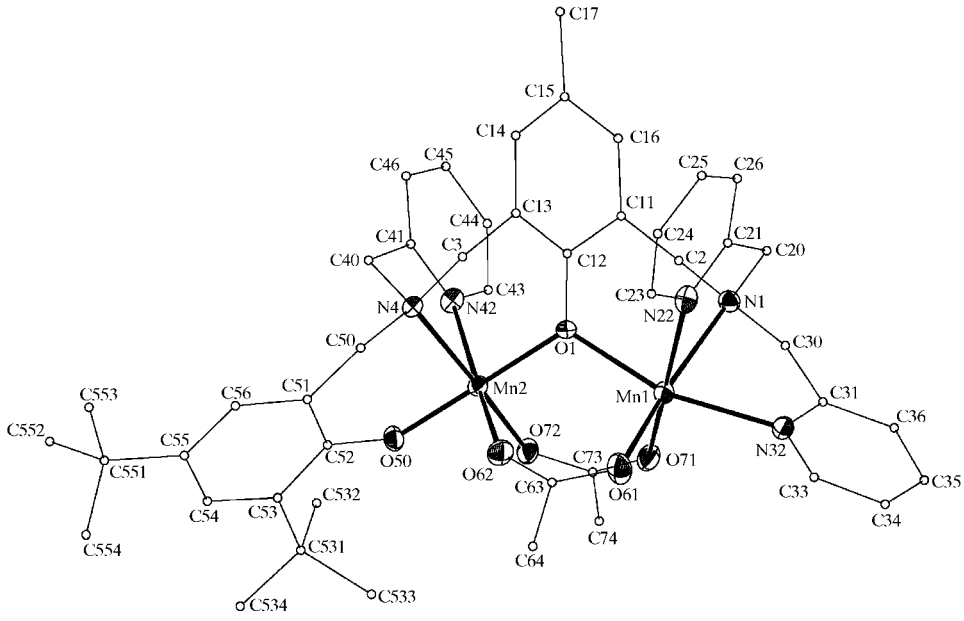


**Figure 1**
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. C atoms are shown as small circles of arbitrary size and H atoms have been omitted for clarity.

the weak *trans* effect of the phenolate group. The longest bond on the $N_3O_3$ side is that to tertiary amine atom N1 [2.335 (3) Å]. This value is rather similar to those found in (II) and (III) [2.313 (2) and 2.279 (3) Å, respectively].

The coordination sphere of Mn2 is complemented by atoms N4 and N42 from the tertiary amine and pyridine group, and atom O50 from the terminal phenolate (hard side). The bond lengths around $Mn^{III}$ (mean 2.041 Å) are quite similar to those found in (II) (mean 2.052 Å), and the longer axial bond lengths [Mn2—N42 = 2.278 (3) Å and Mn2—O62 = 2.129 (3) Å] are consistent with a Jahn–Teller distortion of this high-spin $d^4$ ion. The terminal $Mn^{III}—O_{phenolate}$ bond [1.825 (3) Å] and Mn···Mn distance [3.466 (1) Å] are slightly shorter than those found in (II) [1.852 (2) and 3.497 Å, respectively], as expected, due to the effect caused by the *tert*-butyl substituents.

The Mn1—O1—Mn2 bridging angle of 116.8 (1)° falls within the range found for similarly coordinated mixed-valence manganese dimers with the structural $[Mn^{III}Mn^{II}(\mu$-phenoxo$)(\mu$-OAc$)_2]$ unit. In (II), this angle is 116.6°, in $[Mn_2(L\text{-Im})(\mu\text{-OAc})_2]^+$ it is 116.8° [HL-Im is 2,6-bis({bis[(1-methylimidazol-2-yl)methyl]amino}methyl)-4-methylphenol; Buchanan *et al.*, 1988], in $[Mn_2(bpmp)(\mu\text{-OAc})_2]^+$ it is 114.4° {Hbpmp is 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol; Diril *et al.*, 1989} and in $[Mn_2(\mu\text{-}L)(\mu\text{-OAc})_2(H_2O)]^{2+}$ it is 115.59° {HL is 2-[*N*-bis(2-pyridylmethyl)-aminomethyl]-6-[*N*-(benzyl)(2-pyridylmethyl)aminomethyl]-4-methylphenol; Dubois *et al.*, 2003}.

Redox potentials are strongly dependent on the electronic character of the ligand substituent and on the asymmetry of the ligand. It is interesting to note that, despite the similarities of the averaged bond lengths and angles in the isostructural complexes (I) and (II), the $E_{1/2}$ value of the redox couple $[Mn^{II}Mn^{III}]/[Mn^{II}Mn^{II}]$ is cathodically shifted by 55 mV, a result which is consistent with the electron-donating effect of the *tert*-butyl groups and the slightly shorter $Mn^{III}—O_{phenolate}$ bond length in complex (I), as described above. As reported by Miyasaka *et al.* (2003), the redox potentials can exhibit a linear correlation with the Hammett substituent constant $\sigma_p$.

In summary, a new unsymmetrical mixed-valence $Mn^{II}$–$Mn^{III}$ complex has been structurally characterized and provides the possibility of studies of peroxide disproportionation and of correlating the redox potential and ligand field contribution to the rate and efficiency of this catalytic process.

## Experimental

The ligand $H_2$Ldtb was prepared as follows. To a solution of 2-[bis-(2-pyridylmethyl)aminomethyl]-6-[(2-pyridylmethyl)aminomethyl]-4-methylphenol (Greatti *et al.*, 2004) (3.4 g, 8 mmol) in dichloromethane, triethylamine (1.21 g, 12 mmol) and 4,6-di-*tert*-butyl-2-(chloromethyl)phenol (Sokolowski *et al.*, 1997) (3.02 g, 12 mmol) were added. The resulting mixture was allowed to react for 24 h while being stirred at room temperature. The product was extracted with aqueous $NaHCO_3$ solution (8 × 50 ml). The organic layers were dried over $Na_2SO_4$, the solvent was removed under reduced pressure and a pale-yellow solid was obtained (4.65 g, 7.2 mmol, yield 90%). $^1$H NMR ($CDCl_3$): $\delta$ 8.54, 7.61, 7.53, 7.15, 6.97, 6.84 (16H, aromatic H), 3.92, 3.85, 3.84, 3.80 (*s*, 12H, $CH_2$), 2.23 (*s*, $CH_3$), 1.42, 1.25 (*s*, *tert*-butyl). Complex (I) was prepared by adding $Mn(OAc)_2{\cdot}4H_2O$ (1.0 mmol) and NaOAc (1.0 mmol) to a methanolic solution of the ligand $H_2$Ldtb (0.5 mmol) with stirring at 313 K for 20 min. The solution immediately turned dark red and then $NaBPh_4$ (0.5 mmol) was added. After slow evaporation of the solvent, dark-red crystals of (I) suitable for X-ray analysis were isolated (yield 82%).

*Crystal data*

$[Mn_2(C_{42}H_{49}N_5O_2)(C_2H_3O_2)_2]\cdot(C_{24}H_{20}B)$
$M_r = 1203.04$
Monoclinic, $P2_1/n$
$a = 16.492$ (3) Å
$b = 16.804$ (3) Å
$c = 24.519$ (5) Å
$\beta = 109.07$ (3)°
$V = 6422$ (2) Å$^3$
$Z = 4$
$D_x = 1.244$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.9$–$13.2°$
$\mu = 0.45$ mm$^{-1}$
$T = 293$ (2) K
Irregular block, dark red
0.47 × 0.40 × 0.13 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan [(North *et al.*, 1968) and *PLATON* (Spek, 2003)]
$T_{min} = 0.829$, $T_{max} = 0.937$
11638 measured reflections
11223 independent reflections
4980 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 19$
$k = -19 \rightarrow 0$
$l = -29 \rightarrow 27$
3 standard reflections
every 200 reflections
intensity decay: 1%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.127$
$S = 0.86$
11223 reflections
784 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{min} = -0.31$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Mn1—O61 | 2.067 (3) | Mn2—O50 | 1.823 (2) |
| Mn1—O71 | 2.139 (3) | Mn2—O1 | 1.905 (2) |
| Mn1—O1 | 2.161 (2) | Mn2—O72 | 1.984 (3) |
| Mn1—N32 | 2.237 (3) | Mn2—N4 | 2.118 (3) |
| Mn1—N22 | 2.262 (4) | Mn2—O62 | 2.129 (3) |
| Mn1—N1 | 2.335 (3) | Mn2—N42 | 2.278 (3) |
| | | | |
| O61—Mn1—O71 | 97.80 (13) | O50—Mn2—O72 | 86.59 (11) |
| O61—Mn1—O1 | 100.42 (11) | O1—Mn2—O72 | 92.36 (10) |
| O71—Mn1—O1 | 88.22 (10) | O50—Mn2—N4 | 88.71 (11) |
| O61—Mn1—N32 | 101.59 (13) | O1—Mn2—N4 | 91.88 (11) |
| O71—Mn1—N32 | 87.95 (11) | O72—Mn2—N4 | 167.14 (12) |
| O1—Mn1—N32 | 157.97 (11) | O50—Mn2—O62 | 92.03 (12) |
| O61—Mn1—N22 | 96.88 (14) | O1—Mn2—O62 | 90.15 (11) |
| O71—Mn1—N22 | 164.95 (13) | O72—Mn2—O62 | 97.88 (12) |
| O1—Mn1—N22 | 85.85 (10) | N4—Mn2—O62 | 94.24 (11) |
| N32—Mn1—N22 | 92.38 (12) | O50—Mn2—N42 | 91.52 (12) |
| O61—Mn1—N1 | 169.30 (13) | O1—Mn2—N42 | 86.42 (11) |
| O71—Mn1—N1 | 91.08 (11) | O72—Mn2—N42 | 89.94 (12) |
| O1—Mn1—N1 | 85.76 (10) | N4—Mn2—N42 | 78.22 (12) |
| N32—Mn1—N1 | 72.64 (12) | O62—Mn2—N42 | 171.59 (12) |
| N22—Mn1—N1 | 74.71 (13) | Mn2—O1—Mn1 | 116.74 (11) |
| O50—Mn2—O1 | 177.69 (12) | | |

The crystals of (I) grew from the mother solution as large prisms, but these diffracted poorly. Thus, the number of observed reflections in the *hkl* file is small (44%), giving rise to the consistency values $R_{int} = 0.0518$ and $R_\sigma = 0.1572$. One *tert*-butyl group is disordered and its terminal C atoms have two alternative positions, with occupancy factors of 0.7 and 0.3. Some non-H atoms show abnormally high displacement parameters, but all these atoms were refined with anisotropic displacement parameters, with a positive definite thermal tensor. This gives high $U_{eq}$(max):$U_{eq}$(min) ratios for C and H atoms. H atoms were added in their calculated positions and included in the structure-factor calculations, with C—H distances of 0.93–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for methyl atoms.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* in *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1508). Services for accessing these data are described at the back of the journal.

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