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# Tetraethylammonium [12,12-diethyl-2,2,9,9-tetramethyl-1,4,7,10-tetraza-5,6-benzotridecane-3,8,11,13-tetraone(4−)]oxidomanganate(V)

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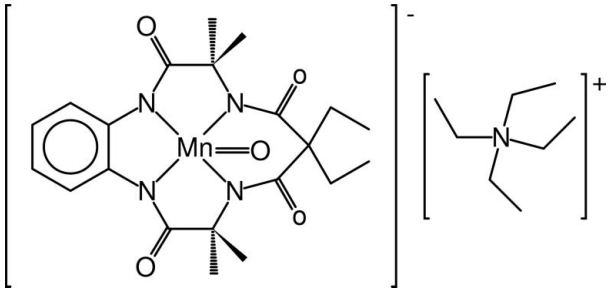
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.044; $wR$ factor = 0.073; data-to-parameter ratio = 15.1.

The $Mn^V$ complex in the title compound, $(C_8H_{20}N)[Mn(C_{21}H_{26}N_4O_4)O]$, is interesting as it has been suggested that $Mn^V$ oxospecies are intermediates both in epoxidation of alkenes and in water oxidation in PSII, *i.e.* photosystem II, the protein found in oxygenic photosynthetic organisms, which uses light to split water into $O_2$, protons and electrons. The Mn atom has a square-pyramidal coordination of four N atoms with an apical O atom. The four N atoms coordinating to Mn [Mn—N = 1.872 (2)–1.882 (2) Å] form a plane within 0.03 (3) Å from which the Mn ion is displaced by 0.582 (2) Å.

## Related literature

For general background, see: Collins *et al.* (1990, 1991); Cavallo & Jacobsen (2003); Linde *et al.* (1999). For the use of similar compounds as model compounds in PSII, see: Weng *et al.* (2004). The oxidation state of the Mn atom was verified according to Brown & Altermatt (1985) and Brown (1996).



## Experimental

### Crystal data

$(C_8H_{20}N)[Mn(C_{21}H_{26}N_4O_4)O]$
$M_r$ = 599.65
Monoclinic, $P2_1/c$
$a$ = 11.2606 (11) Å
$b$ = 15.5269 (15) Å
$c$ = 17.7586 (17) Å
$\beta$ = 96.024 (8)°
$V$ = 3087.8 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.47 mm$^{-1}$
$T$ = 293 (2) K
0.20 × 0.15 × 0.10 mm

### Data collection

Oxford Diffraction Xcalibur-3 $\kappa$ diffractometer with SapphireIII CCD
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
$T_{min}$ = 0.899, $T_{max}$ = 0.960
18232 measured reflections
5454 independent reflections
2197 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.078

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.074
$S$ = 0.82
5454 reflections
361 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| N1—Mn | 1.872 (2) | N4—Mn | 1.882 (2) |
| N2—Mn | 1.874 (2) | O5—Mn | 1.561 (2) |
| N3—Mn | 1.879 (2) | | |
| O5—Mn—N1 | 109.08 (10) | N2—Mn—N3 | 79.91 (12) |
| O5—Mn—N2 | 107.12 (10) | O5—Mn—N4 | 107.30 (10) |
| N1—Mn—N2 | 82.09 (12) | N1—Mn—N4 | 93.50 (12) |
| O5—Mn—N3 | 108.91 (10) | N2—Mn—N4 | 144.80 (11) |
| N1—Mn—N3 | 141.27 (11) | N3—Mn—N4 | 82.27 (12) |

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2305).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m2672-m2673 [ **doi:10.1107/S1600536807047691** ]

# Tetraethylammonium [12,12-diethyl-2,2,9,9-tetramethyl-1,4,7,10-tetraza-5,6-benzotridecane-3,8,11,13-tetraone(4-)]oxidomanganate(V)

**G. Berggren, F. B. Kaynak, M. F. Anderlund, L. Eriksson and B. Åkermark**

## Comment

The title complex was prepared with the intention of testing a mechanism for oxygen-transfer discussed by *e.g.* Cavallo & Jacobsen (2003) as well as Linde *et al.* (1999) were the spin-state of the Mn-oxo species is supposed to dictate whether the reaction will proceed *via* a radical (from the triplet state) or metallacyclic intermediate (from the quintet-state). Since the title compound is isolated in a stable singlet-state it might be possible to selectively excite it to form either one or possibly both of these spin-states. Similar compounds have also been used as model complexes in the study of the water oxidizing enzyme, PSII (Weng *et al.*, 2004). The oxidation state of the $Mn^{V}$ atom was verified with bond valence calculations (Brown & Altermatt, 1985; Brown, 1996).

## Experimental

The title compound was synthesized following literature procedures (Collins *et al.*, 1990; 1991) and recrystallized from a $CH_2Cl_2$ solution by adding benzene as a layer upon the original solution and letting the benzene mix with the original solution by diffusion.

## Refinement

All hydrogen atoms were geometrically positioned (C—H 0.93–0.97 Å) and refined in riding mode approximation, with $U_{iso}(H) = 1.5U_{eq}(C)$ for the $CH_3$ and $1.2U_{eq}(C)$ for the $CH_2$ and aromatic CH.

## Figures

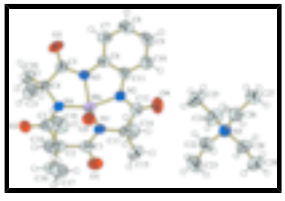


Fig. 1. The content of asymmetric part of the title compound with the atom numbering scheme and displacement ellipsoids drawn at the 50% probability level.

## Tetraethylammonium [12,12-diethyl-2,2,9,9,-tetramethyl-1,4,7,10-tetraza-5,6-benzotridecane- 3,8,11,13-tetraone(4-)]oxidomanganate(V)

*Crystal data*

| | |
|---|---|
| $(C_8H_{20}N)[Mn(C_{21}H_{26}N_4O_4)O]$ | $Z = 4$ |
| $M_r = 599.65$ | $F_{000} = 1280$ |
| Monoclinic, $P2_1/c$ | $D_x = 1.290$ Mg m$^{-3}$ |

| | |
|---|---|
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation<br>$\lambda$ = 0.71073 Å |
| $a$ = 11.2606 (11) Å | $\theta$ = 3.8–33.4º |
| $b$ = 15.5269 (15) Å | $\mu$ = 0.47 mm$^{-1}$ |
| $c$ = 17.7586 (17) Å | $T$ = 293 (2) K |
| $\beta$ = 96.024 (8)º | Prism, red |
| $V$ = 3087.8 (5) Å$^3$ | 0.20 × 0.15 × 0.10 mm |

*Data collection*

| | |
|---|---|
| Oxford Diffraction Xcalibur-3 kappa diffractometer with SapphireIII CCD | 5454 independent reflections |
| Radiation source: fine-focus sealed tube | 2197 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.078 |
| Detector resolution: 12 pixels mm$^{-1}$ | $\theta_{max}$ = 25.0º |
| $T$ = 293(2) K | $\theta_{min}$ = 1.8º |
| $\omega$ scans at different $\varphi$ | $h$ = −13→13 |
| Absorption correction: numerical (X-RED; Stoe & Cie, 1997) | $k$ = −18→18 |
| $T_{min}$ = 0.899, $T_{max}$ = 0.960 | $l$ = −21→21 |
| 18232 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.044 | H-atom parameters constrained |
| $wR(F^2)$ = 0.074 | $w = 1/[\sigma^2(F_o^2) + (0.0259P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 0.82 | $(\Delta/\sigma)_{max} < 0.001$ |
| 5454 reflections | $\Delta\rho_{max}$ = 0.24 e Å$^{-3}$ |
| 361 parameters | $\Delta\rho_{min}$ = −0.26 e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit S are based on $F^2$, conventional $R$-factors $R$ are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.0713 (3) | 0.1659 (2) | 0.64612 (19) | 0.0536 (10) |
| C2 | −0.0228 (3) | 0.1642 (2) | 0.70234 (19) | 0.0494 (9) |
| C3 | 0.0040 (4) | 0.1197 (2) | 0.77932 (18) | 0.0487 (10) |
| C4 | 0.1351 (3) | 0.0566 (2) | 0.88100 (16) | 0.0473 (9) |
| C5 | 0.2652 (3) | 0.0322 (2) | 0.89271 (19) | 0.0566 (10) |
| C6 | 0.4369 (3) | 0.00699 (19) | 0.82099 (19) | 0.0470 (9) |
| C7 | 0.5237 (3) | −0.0231 (2) | 0.87699 (19) | 0.0574 (10) |
| H7 | 0.5044 | −0.0341 | 0.9257 | 0.069* |
| C8 | 0.6371 (3) | −0.0360 (2) | 0.8587 (2) | 0.0671 (11) |
| H8 | 0.6950 | −0.0555 | 0.8960 | 0.080* |
| C9 | 0.6687 (3) | −0.0210 (2) | 0.7866 (2) | 0.0698 (12) |
| H9 | 0.7465 | −0.0312 | 0.7757 | 0.084* |
| C10 | 0.5833 (3) | 0.0093 (2) | 0.73066 (19) | 0.0575 (10) |
| H10 | 0.6033 | 0.0198 | 0.6820 | 0.069* |
| C11 | 0.4679 (3) | 0.0237 (2) | 0.74835 (19) | 0.0474 (9) |
| C12 | 0.3802 (4) | 0.0999 (2) | 0.63519 (19) | 0.0578 (11) |
| C13 | 0.2646 (3) | 0.1429 (2) | 0.60455 (18) | 0.0539 (10) |
| C14 | 0.2923 (3) | 0.2382 (2) | 0.59448 (17) | 0.0780 (12) |
| H14A | 0.2208 | 0.2679 | 0.5750 | 0.117* |
| H14B | 0.3514 | 0.2442 | 0.5596 | 0.117* |
| H14C | 0.3221 | 0.2625 | 0.6425 | 0.117* |
| C15 | 0.2206 (3) | 0.0987 (2) | 0.52830 (16) | 0.0861 (13) |
| H15A | 0.1475 | 0.1250 | 0.5072 | 0.129* |
| H15B | 0.2072 | 0.0386 | 0.5369 | 0.129* |
| H15C | 0.2801 | 0.1050 | 0.4937 | 0.129* |
| C16 | −0.1365 (3) | 0.1231 (2) | 0.66216 (18) | 0.0666 (11) |
| H16A | −0.1984 | 0.1242 | 0.6963 | 0.080* |
| H16B | −0.1639 | 0.1579 | 0.6183 | 0.080* |
| C17 | −0.1203 (3) | 0.0311 (2) | 0.63653 (18) | 0.0866 (12) |
| H17A | −0.1945 | 0.0099 | 0.6119 | 0.130* |
| H17B | −0.0955 | −0.0042 | 0.6797 | 0.130* |
| H17C | −0.0606 | 0.0295 | 0.6018 | 0.130* |
| C18 | −0.0493 (3) | 0.2593 (2) | 0.72047 (19) | 0.0738 (12) |
| H18A | −0.0758 | 0.2890 | 0.6736 | 0.089* |
| H18B | −0.1142 | 0.2612 | 0.7523 | 0.089* |
| C19 | 0.0576 (4) | 0.3070 (2) | 0.7601 (2) | 0.0905 (14) |
| H19A | 0.0354 | 0.3653 | 0.7697 | 0.136* |
| H19B | 0.1216 | 0.3066 | 0.7285 | 0.136* |
| H19C | 0.0831 | 0.2790 | 0.8073 | 0.136* |
| C20 | 0.1145 (3) | 0.1258 (2) | 0.93946 (15) | 0.0658 (11) |
| H20A | 0.0320 | 0.1427 | 0.9338 | 0.099* |
| H20B | 0.1636 | 0.1750 | 0.9318 | 0.099* |
| H20C | 0.1351 | 0.1034 | 0.9895 | 0.099* |
| C21 | 0.0643 (3) | −0.0252 (2) | 0.89443 (17) | 0.0766 (12) |
| H21A | −0.0196 | −0.0126 | 0.8878 | 0.115* |

| | | | | |
|---|---|---|---|---|
| H21B | 0.0860 | −0.0456 | 0.9450 | 0.115* |
| H21C | 0.0820 | −0.0687 | 0.8589 | 0.115* |
| N1 | 0.1796 (3) | 0.12924 (16) | 0.66200 (13) | 0.0449 (7) |
| N2 | 0.3707 (2) | 0.05739 (16) | 0.70151 (14) | 0.0455 (7) |
| N3 | 0.3167 (2) | 0.02626 (15) | 0.82645 (13) | 0.0447 (7) |
| N4 | 0.1136 (2) | 0.08759 (15) | 0.80135 (13) | 0.0429 (7) |
| O3 | 0.3189 (2) | 0.01663 (18) | 0.95520 (12) | 0.1030 (10) |
| O4 | 0.4708 (2) | 0.10505 (17) | 0.60263 (13) | 0.0946 (10) |
| O5 | 0.16898 (18) | −0.04408 (13) | 0.70485 (9) | 0.0552 (6) |
| O1 | 0.0409 (2) | 0.20457 (16) | 0.58588 (13) | 0.0806 (8) |
| O2 | −0.0786 (2) | 0.11887 (14) | 0.82048 (12) | 0.0658 (7) |
| Mn | 0.21949 (5) | 0.04441 (3) | 0.73523 (2) | 0.04636 (17) |
| N5 | 0.6263 (3) | 0.24009 (18) | 0.40445 (14) | 0.0504 (8) |
| C22 | 0.5082 (3) | 0.1965 (2) | 0.40647 (19) | 0.0751 (12) |
| H22A | 0.5030 | 0.1753 | 0.4574 | 0.090* |
| H22B | 0.5053 | 0.1470 | 0.3730 | 0.090* |
| C23 | 0.3988 (3) | 0.2534 (3) | 0.3835 (2) | 0.1245 (18) |
| H23A | 0.3273 | 0.2204 | 0.3862 | 0.187* |
| H23B | 0.4016 | 0.2736 | 0.3326 | 0.187* |
| H23C | 0.3991 | 0.3017 | 0.4172 | 0.187* |
| C24 | 0.6415 (4) | 0.3134 (2) | 0.46178 (18) | 0.0798 (13) |
| H24A | 0.7159 | 0.3428 | 0.4558 | 0.096* |
| H24B | 0.5772 | 0.3544 | 0.4499 | 0.096* |
| C25 | 0.6422 (4) | 0.2870 (2) | 0.54408 (16) | 0.0951 (14) |
| H25A | 0.6528 | 0.3371 | 0.5758 | 0.143* |
| H25B | 0.7066 | 0.2474 | 0.5571 | 0.143* |
| H25C | 0.5678 | 0.2598 | 0.5514 | 0.143* |
| C26 | 0.7197 (3) | 0.1717 (2) | 0.42219 (18) | 0.0657 (11) |
| H26A | 0.7043 | 0.1438 | 0.4691 | 0.079* |
| H26B | 0.7098 | 0.1286 | 0.3825 | 0.079* |
| C27 | 0.8479 (3) | 0.2010 (3) | 0.43007 (19) | 0.0993 (14) |
| H27A | 0.8994 | 0.1524 | 0.4414 | 0.149* |
| H27B | 0.8603 | 0.2423 | 0.4703 | 0.149* |
| H27C | 0.8659 | 0.2270 | 0.3835 | 0.149* |
| C28 | 0.6357 (3) | 0.2807 (2) | 0.32739 (16) | 0.0650 (11) |
| H28A | 0.5786 | 0.3276 | 0.3206 | 0.078* |
| H28B | 0.7148 | 0.3054 | 0.3274 | 0.078* |
| C29 | 0.6142 (3) | 0.2206 (2) | 0.26035 (16) | 0.0801 (13) |
| H29A | 0.6226 | 0.2518 | 0.2146 | 0.120* |
| H29B | 0.5350 | 0.1973 | 0.2584 | 0.120* |
| H29C | 0.6714 | 0.1746 | 0.2656 | 0.120* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.054 (3) | 0.056 (3) | 0.048 (2) | −0.004 (2) | −0.007 (2) | 0.0051 (19) |
| C2 | 0.046 (3) | 0.044 (3) | 0.056 (2) | 0.000 (2) | −0.004 (2) | −0.0021 (19) |
| C3 | 0.058 (3) | 0.043 (2) | 0.044 (2) | −0.001 (2) | 0.001 (2) | −0.0091 (18) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C4 | 0.047 (2) | 0.055 (3) | 0.039 (2) | 0.010 (2) | 0.0029 (18) | 0.0039 (19) |
| C5 | 0.054 (3) | 0.071 (3) | 0.044 (2) | 0.013 (2) | 0.003 (2) | 0.001 (2) |
| C6 | 0.047 (3) | 0.044 (2) | 0.049 (2) | 0.000 (2) | −0.001 (2) | −0.0018 (18) |
| C7 | 0.055 (3) | 0.059 (3) | 0.055 (2) | 0.003 (2) | −0.006 (2) | 0.0045 (19) |
| C8 | 0.052 (3) | 0.070 (3) | 0.076 (3) | 0.007 (3) | −0.009 (2) | 0.004 (2) |
| C9 | 0.042 (3) | 0.078 (3) | 0.090 (3) | 0.005 (2) | 0.009 (3) | −0.011 (2) |
| C10 | 0.051 (3) | 0.063 (3) | 0.059 (2) | −0.002 (2) | 0.008 (2) | −0.0031 (19) |
| C11 | 0.039 (2) | 0.049 (3) | 0.054 (2) | 0.001 (2) | 0.004 (2) | −0.0086 (19) |
| C12 | 0.058 (3) | 0.067 (3) | 0.049 (2) | 0.000 (2) | 0.010 (2) | −0.001 (2) |
| C13 | 0.058 (3) | 0.062 (3) | 0.041 (2) | −0.001 (2) | 0.000 (2) | 0.0075 (19) |
| C14 | 0.082 (3) | 0.073 (3) | 0.080 (3) | −0.006 (3) | 0.008 (2) | 0.029 (2) |
| C15 | 0.097 (3) | 0.117 (3) | 0.043 (2) | −0.008 (3) | 0.004 (2) | −0.006 (2) |
| C16 | 0.056 (3) | 0.076 (3) | 0.064 (2) | 0.003 (3) | −0.009 (2) | 0.003 (2) |
| C17 | 0.079 (3) | 0.095 (4) | 0.082 (3) | −0.020 (3) | −0.006 (2) | −0.021 (3) |
| C18 | 0.072 (3) | 0.060 (3) | 0.087 (3) | 0.012 (3) | −0.002 (3) | 0.005 (2) |
| C19 | 0.084 (3) | 0.056 (3) | 0.129 (4) | −0.003 (3) | −0.005 (3) | −0.015 (3) |
| C20 | 0.067 (3) | 0.090 (3) | 0.041 (2) | −0.001 (2) | 0.007 (2) | −0.013 (2) |
| C21 | 0.095 (3) | 0.072 (3) | 0.063 (2) | −0.007 (3) | 0.012 (2) | 0.009 (2) |
| N1 | 0.0452 (19) | 0.0511 (19) | 0.0373 (16) | 0.0060 (17) | −0.0008 (15) | 0.0063 (13) |
| N2 | 0.0458 (19) | 0.0526 (19) | 0.0380 (15) | 0.0024 (17) | 0.0044 (15) | 0.0053 (15) |
| N3 | 0.0414 (19) | 0.053 (2) | 0.0387 (16) | 0.0088 (16) | −0.0007 (14) | 0.0012 (14) |
| N4 | 0.043 (2) | 0.051 (2) | 0.0339 (15) | 0.0022 (16) | 0.0008 (15) | 0.0016 (13) |
| O3 | 0.090 (2) | 0.176 (3) | 0.0399 (14) | 0.044 (2) | −0.0057 (14) | 0.0171 (16) |
| O4 | 0.074 (2) | 0.134 (2) | 0.0805 (19) | 0.0175 (19) | 0.0307 (18) | 0.0368 (17) |
| O5 | 0.0587 (15) | 0.0472 (14) | 0.0583 (13) | −0.0089 (14) | −0.0008 (11) | −0.0127 (13) |
| O1 | 0.072 (2) | 0.102 (2) | 0.0652 (16) | 0.0138 (17) | −0.0053 (15) | 0.0302 (15) |
| O2 | 0.0459 (16) | 0.0950 (19) | 0.0568 (15) | 0.0063 (15) | 0.0070 (13) | 0.0018 (14) |
| Mn | 0.0484 (3) | 0.0494 (4) | 0.0399 (3) | 0.0004 (3) | −0.0018 (2) | −0.0004 (3) |
| N5 | 0.059 (2) | 0.041 (2) | 0.0513 (18) | 0.0051 (18) | 0.0048 (16) | 0.0071 (15) |
| C22 | 0.060 (3) | 0.095 (3) | 0.071 (3) | 0.000 (3) | 0.011 (2) | 0.017 (2) |
| C23 | 0.062 (3) | 0.193 (5) | 0.121 (4) | 0.028 (4) | 0.017 (3) | 0.043 (3) |
| C24 | 0.115 (4) | 0.052 (3) | 0.071 (3) | 0.012 (3) | 0.002 (3) | −0.006 (2) |
| C25 | 0.139 (4) | 0.098 (3) | 0.047 (2) | 0.019 (3) | 0.006 (3) | −0.010 (2) |
| C26 | 0.069 (3) | 0.063 (3) | 0.065 (2) | 0.014 (3) | 0.008 (2) | 0.007 (2) |
| C27 | 0.062 (3) | 0.159 (4) | 0.075 (3) | 0.004 (3) | −0.003 (2) | 0.021 (3) |
| C28 | 0.074 (3) | 0.067 (3) | 0.054 (2) | 0.001 (2) | 0.001 (2) | 0.019 (2) |
| C29 | 0.089 (3) | 0.098 (3) | 0.052 (2) | −0.003 (3) | 0.002 (2) | 0.000 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—O1 | 1.243 (3) | C18—H18A | 0.9700 |
| C1—N1 | 1.348 (4) | C18—H18B | 0.9700 |
| C1—C2 | 1.531 (4) | C19—H19A | 0.9600 |
| C2—C3 | 1.533 (4) | C19—H19B | 0.9600 |
| C2—C16 | 1.537 (4) | C19—H19C | 0.9600 |
| C2—C18 | 1.548 (4) | C20—H20A | 0.9600 |
| C3—O2 | 1.242 (3) | C20—H20B | 0.9600 |
| C3—N4 | 1.350 (4) | C20—H20C | 0.9600 |
| C4—N4 | 1.490 (3) | C21—H21A | 0.9600 |

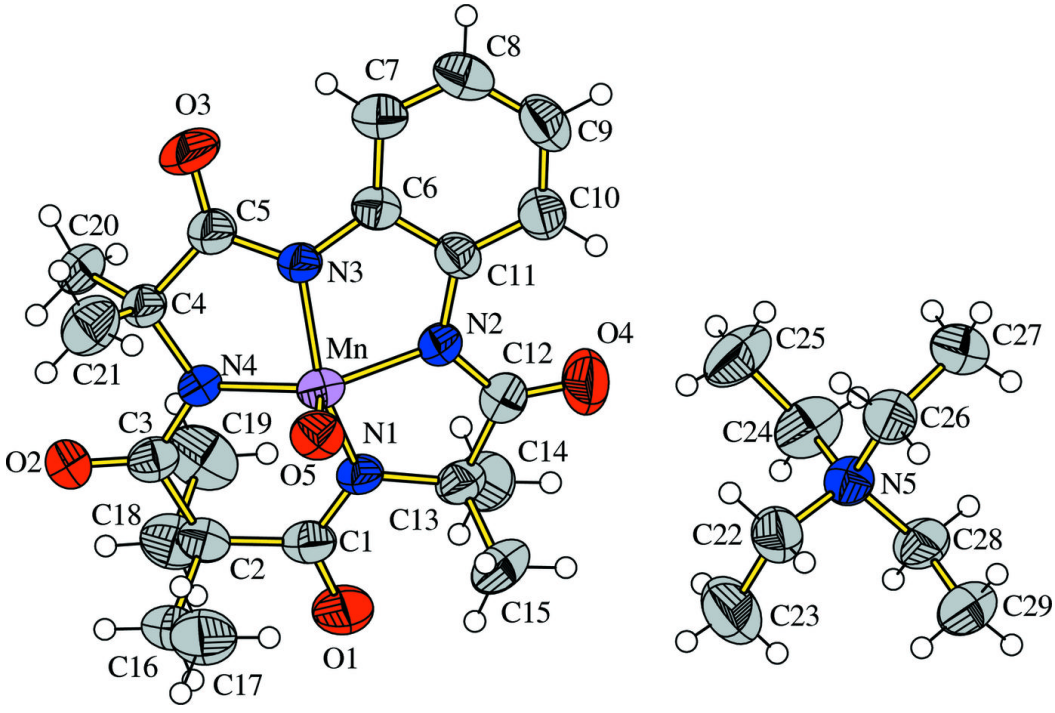
| | | | |
|---|---|---|---|
| C4—C5 | 1.507 (4) | C21—H21B | 0.9600 |
| C4—C20 | 1.529 (4) | C21—H21C | 0.9600 |
| C4—C21 | 1.531 (4) | N1—Mn | 1.872 (2) |
| C5—O3 | 1.231 (3) | N2—Mn | 1.874 (2) |
| C5—N3 | 1.369 (3) | N3—Mn | 1.879 (2) |
| C6—C11 | 1.396 (4) | N4—Mn | 1.882 (2) |
| C6—N3 | 1.399 (4) | O5—Mn | 1.561 (2) |
| C6—C7 | 1.399 (4) | N5—C22 | 1.495 (4) |
| C7—C8 | 1.365 (4) | N5—C26 | 1.505 (4) |
| C7—H7 | 0.9300 | N5—C28 | 1.521 (3) |
| C8—C9 | 1.384 (4) | N5—C24 | 1.525 (4) |
| C8—H8 | 0.9300 | C22—C23 | 1.536 (4) |
| C9—C10 | 1.391 (4) | C22—H22A | 0.9700 |
| C9—H9 | 0.9300 | C22—H22B | 0.9700 |
| C10—C11 | 1.386 (4) | C23—H23A | 0.9600 |
| C10—H10 | 0.9300 | C23—H23B | 0.9600 |
| C11—N2 | 1.405 (4) | C23—H23C | 0.9600 |
| C12—O4 | 1.227 (4) | C24—C25 | 1.517 (4) |
| C12—N2 | 1.364 (4) | C24—H24A | 0.9700 |
| C12—C13 | 1.513 (4) | C24—H24B | 0.9700 |
| C13—N1 | 1.486 (4) | C25—H25A | 0.9600 |
| C13—C14 | 1.526 (4) | C25—H25B | 0.9600 |
| C13—C15 | 1.552 (4) | C25—H25C | 0.9600 |
| C14—H14A | 0.9600 | C26—C27 | 1.507 (4) |
| C14—H14B | 0.9600 | C26—H26A | 0.9700 |
| C14—H14C | 0.9600 | C26—H26B | 0.9700 |
| C15—H15A | 0.9600 | C27—H27A | 0.9600 |
| C15—H15B | 0.9600 | C27—H27B | 0.9600 |
| C15—H15C | 0.9600 | C27—H27C | 0.9600 |
| C16—C17 | 1.516 (4) | C28—C29 | 1.512 (4) |
| C16—H16A | 0.9700 | C28—H28A | 0.9700 |
| C16—H16B | 0.9700 | C28—H28B | 0.9700 |
| C17—H17A | 0.9600 | C29—H29A | 0.9600 |
| C17—H17B | 0.9600 | C29—H29B | 0.9600 |
| C17—H17C | 0.9600 | C29—H29C | 0.9600 |
| C18—C19 | 1.521 (4) | | |
| O1—C1—N1 | 123.1 (3) | H20A—C20—H20B | 109.5 |
| O1—C1—C2 | 115.0 (3) | C4—C20—H20C | 109.5 |
| N1—C1—C2 | 121.9 (3) | H20A—C20—H20C | 109.5 |
| C1—C2—C3 | 120.3 (3) | H20B—C20—H20C | 109.5 |
| C1—C2—C16 | 107.8 (3) | C4—C21—H21A | 109.5 |
| C3—C2—C16 | 107.7 (3) | C4—C21—H21B | 109.5 |
| C1—C2—C18 | 106.3 (3) | H21A—C21—H21B | 109.5 |
| C3—C2—C18 | 105.6 (3) | C4—C21—H21C | 109.5 |
| C16—C2—C18 | 108.8 (3) | H21A—C21—H21C | 109.5 |
| O2—C3—N4 | 123.0 (3) | H21B—C21—H21C | 109.5 |
| O2—C3—C2 | 116.1 (3) | C1—N1—C13 | 115.4 (3) |
| N4—C3—C2 | 120.9 (3) | C1—N1—Mn | 126.1 (2) |
| N4—C4—C5 | 105.7 (3) | C13—N1—Mn | 116.9 (2) |

| | | | |
|---|---|---|---|
| N4—C4—C20 | 113.3 (3) | C12—N2—C11 | 124.3 (3) |
| C5—C4—C20 | 107.3 (3) | C12—N2—Mn | 119.0 (2) |
| N4—C4—C21 | 112.4 (3) | C11—N2—Mn | 116.7 (2) |
| C5—C4—C21 | 106.6 (3) | C5—N3—C6 | 125.0 (3) |
| C20—C4—C21 | 111.0 (3) | C5—N3—Mn | 118.0 (2) |
| O3—C5—N3 | 123.3 (3) | C6—N3—Mn | 116.9 (2) |
| O3—C5—C4 | 123.5 (3) | C3—N4—C4 | 116.5 (3) |
| N3—C5—C4 | 113.1 (3) | C3—N4—Mn | 124.8 (2) |
| C11—C6—N3 | 111.2 (3) | C4—N4—Mn | 115.3 (2) |
| C11—C6—C7 | 119.7 (3) | O5—Mn—N1 | 109.08 (10) |
| N3—C6—C7 | 129.1 (3) | O5—Mn—N2 | 107.12 (10) |
| C8—C7—C6 | 118.8 (3) | N1—Mn—N2 | 82.09 (12) |
| C8—C7—H7 | 120.6 | O5—Mn—N3 | 108.91 (10) |
| C6—C7—H7 | 120.6 | N1—Mn—N3 | 141.27 (11) |
| C7—C8—C9 | 122.2 (3) | N2—Mn—N3 | 79.91 (12) |
| C7—C8—H8 | 118.9 | O5—Mn—N4 | 107.30 (10) |
| C9—C8—H8 | 118.9 | N1—Mn—N4 | 93.50 (12) |
| C8—C9—C10 | 119.5 (3) | N2—Mn—N4 | 144.80 (11) |
| C8—C9—H9 | 120.3 | N3—Mn—N4 | 82.27 (12) |
| C10—C9—H9 | 120.3 | C22—N5—C26 | 106.2 (3) |
| C11—C10—C9 | 119.1 (3) | C22—N5—C28 | 110.9 (3) |
| C11—C10—H10 | 120.4 | C26—N5—C28 | 111.6 (3) |
| C9—C10—H10 | 120.4 | C22—N5—C24 | 111.1 (3) |
| C10—C11—C6 | 120.7 (3) | C26—N5—C24 | 111.1 (3) |
| C10—C11—N2 | 128.1 (3) | C28—N5—C24 | 106.1 (2) |
| C6—C11—N2 | 111.2 (3) | N5—C22—C23 | 115.0 (3) |
| O4—C12—N2 | 125.6 (4) | N5—C22—H22A | 108.5 |
| O4—C12—C13 | 121.9 (3) | C23—C22—H22A | 108.5 |
| N2—C12—C13 | 112.4 (3) | N5—C22—H22B | 108.5 |
| N1—C13—C12 | 106.4 (3) | C23—C22—H22B | 108.5 |
| N1—C13—C14 | 111.9 (3) | H22A—C22—H22B | 107.5 |
| C12—C13—C14 | 106.9 (3) | C22—C23—H23A | 109.5 |
| N1—C13—C15 | 111.5 (3) | C22—C23—H23B | 109.5 |
| C12—C13—C15 | 107.5 (3) | H23A—C23—H23B | 109.5 |
| C14—C13—C15 | 112.2 (3) | C22—C23—H23C | 109.5 |
| C13—C14—H14A | 109.5 | H23A—C23—H23C | 109.5 |
| C13—C14—H14B | 109.5 | H23B—C23—H23C | 109.5 |
| H14A—C14—H14B | 109.5 | C25—C24—N5 | 115.5 (3) |
| C13—C14—H14C | 109.5 | C25—C24—H24A | 108.4 |
| H14A—C14—H14C | 109.5 | N5—C24—H24A | 108.4 |
| H14B—C14—H14C | 109.5 | C25—C24—H24B | 108.4 |
| C13—C15—H15A | 109.5 | N5—C24—H24B | 108.4 |
| C13—C15—H15B | 109.5 | H24A—C24—H24B | 107.5 |
| H15A—C15—H15B | 109.5 | C24—C25—H25A | 109.5 |
| C13—C15—H15C | 109.5 | C24—C25—H25B | 109.5 |
| H15A—C15—H15C | 109.5 | H25A—C25—H25B | 109.5 |
| H15B—C15—H15C | 109.5 | C24—C25—H25C | 109.5 |
| C17—C16—C2 | 114.1 (3) | H25A—C25—H25C | 109.5 |
| C17—C16—H16A | 108.7 | H25B—C25—H25C | 109.5 |

| | | | |
|---|---|---|---|
| C2—C16—H16A | 108.7 | C27—C26—N5 | 116.6 (3) |
| C17—C16—H16B | 108.7 | C27—C26—H26A | 108.1 |
| C2—C16—H16B | 108.7 | N5—C26—H26A | 108.1 |
| H16A—C16—H16B | 107.6 | C27—C26—H26B | 108.1 |
| C16—C17—H17A | 109.5 | N5—C26—H26B | 108.1 |
| C16—C17—H17B | 109.5 | H26A—C26—H26B | 107.3 |
| H17A—C17—H17B | 109.5 | C26—C27—H27A | 109.5 |
| C16—C17—H17C | 109.5 | C26—C27—H27B | 109.5 |
| H17A—C17—H17C | 109.5 | H27A—C27—H27B | 109.5 |
| H17B—C17—H17C | 109.5 | C26—C27—H27C | 109.5 |
| C19—C18—C2 | 113.6 (3) | H27A—C27—H27C | 109.5 |
| C19—C18—H18A | 108.9 | H27B—C27—H27C | 109.5 |
| C2—C18—H18A | 108.9 | C29—C28—N5 | 115.6 (3) |
| C19—C18—H18B | 108.9 | C29—C28—H28A | 108.4 |
| C2—C18—H18B | 108.9 | N5—C28—H28A | 108.4 |
| H18A—C18—H18B | 107.7 | C29—C28—H28B | 108.4 |
| C18—C19—H19A | 109.5 | N5—C28—H28B | 108.4 |
| C18—C19—H19B | 109.5 | H28A—C28—H28B | 107.4 |
| H19A—C19—H19B | 109.5 | C28—C29—H29A | 109.5 |
| C18—C19—H19C | 109.5 | C28—C29—H29B | 109.5 |
| H19A—C19—H19C | 109.5 | H29A—C29—H29B | 109.5 |
| H19B—C19—H19C | 109.5 | C28—C29—H29C | 109.5 |
| C4—C20—H20A | 109.5 | H29A—C29—H29C | 109.5 |
| C4—C20—H20B | 109.5 | H29B—C29—H29C | 109.5 |
| O1—C1—C2—C3 | −179.1 (3) | O3—C5—N3—Mn | 175.7 (3) |
| N1—C1—C2—C3 | −0.2 (5) | C4—C5—N3—Mn | −2.3 (4) |
| O1—C1—C2—C16 | 57.1 (4) | C11—C6—N3—C5 | −167.2 (3) |
| N1—C1—C2—C16 | −124.0 (3) | C7—C6—N3—C5 | 11.2 (5) |
| O1—C1—C2—C18 | −59.4 (4) | C11—C6—N3—Mn | 13.3 (3) |
| N1—C1—C2—C18 | 119.5 (3) | C7—C6—N3—Mn | −168.3 (3) |
| C1—C2—C3—O2 | −177.8 (3) | O2—C3—N4—C4 | −4.7 (5) |
| C16—C2—C3—O2 | −54.0 (4) | C2—C3—N4—C4 | 171.9 (3) |
| C18—C2—C3—O2 | 62.2 (4) | O2—C3—N4—Mn | 153.3 (2) |
| C1—C2—C3—N4 | 5.4 (5) | C2—C3—N4—Mn | −30.1 (4) |
| C16—C2—C3—N4 | 129.3 (3) | C5—C4—N4—C3 | −175.0 (3) |
| C18—C2—C3—N4 | −114.6 (3) | C20—C4—N4—C3 | −57.8 (4) |
| N4—C4—C5—O3 | 168.2 (3) | C21—C4—N4—C3 | 69.2 (4) |
| C20—C4—C5—O3 | 47.0 (5) | C5—C4—N4—Mn | 24.9 (3) |
| C21—C4—C5—O3 | −72.1 (4) | C20—C4—N4—Mn | 142.2 (2) |
| N4—C4—C5—N3 | −13.9 (4) | C21—C4—N4—Mn | −90.9 (3) |
| C20—C4—C5—N3 | −135.1 (3) | C1—N1—Mn—O5 | 76.3 (3) |
| C21—C4—C5—N3 | 105.9 (3) | C13—N1—Mn—O5 | −88.5 (2) |
| C11—C6—C7—C8 | −0.5 (5) | C1—N1—Mn—N2 | −178.3 (3) |
| N3—C6—C7—C8 | −178.8 (3) | C13—N1—Mn—N2 | 16.9 (2) |
| C6—C7—C8—C9 | −0.6 (5) | C1—N1—Mn—N3 | −115.4 (3) |
| C7—C8—C9—C10 | 0.9 (5) | C13—N1—Mn—N3 | 79.8 (3) |
| C8—C9—C10—C11 | −0.2 (5) | C1—N1—Mn—N4 | −33.4 (3) |
| C9—C10—C11—C6 | −0.9 (5) | C13—N1—Mn—N4 | 161.8 (2) |
| C9—C10—C11—N2 | 177.0 (3) | C12—N2—Mn—O5 | 93.0 (2) |

| | | | |
|---|---|---|---|
| N3—C6—C11—C10 | 179.8 (3) | C11—N2—Mn—O5 | −88.5 (2) |
| C7—C6—C11—C10 | 1.2 (5) | C12—N2—Mn—N1 | −14.6 (2) |
| N3—C6—C11—N2 | 1.5 (4) | C11—N2—Mn—N1 | 163.9 (2) |
| C7—C6—C11—N2 | −177.0 (3) | C12—N2—Mn—N3 | −160.2 (2) |
| O4—C12—C13—N1 | −175.0 (3) | C11—N2—Mn—N3 | 18.3 (2) |
| N2—C12—C13—N1 | 4.2 (4) | C12—N2—Mn—N4 | −99.4 (3) |
| O4—C12—C13—C14 | −55.3 (4) | C11—N2—Mn—N4 | 79.0 (3) |
| N2—C12—C13—C14 | 124.0 (3) | C5—N3—Mn—O5 | −92.2 (2) |
| O4—C12—C13—C15 | 65.4 (5) | C6—N3—Mn—O5 | 87.3 (2) |
| N2—C12—C13—C15 | −115.3 (3) | C5—N3—Mn—N1 | 99.5 (3) |
| C1—C2—C16—C17 | 61.3 (4) | C6—N3—Mn—N1 | −81.0 (3) |
| C3—C2—C16—C17 | −69.8 (4) | C5—N3—Mn—N2 | 163.0 (2) |
| C18—C2—C16—C17 | 176.2 (3) | C6—N3—Mn—N2 | −17.4 (2) |
| C1—C2—C18—C19 | −63.9 (4) | C5—N3—Mn—N4 | 13.5 (2) |
| C3—C2—C18—C19 | 65.0 (4) | C6—N3—Mn—N4 | −166.9 (2) |
| C16—C2—C18—C19 | −179.7 (3) | C3—N4—Mn—O5 | −72.7 (3) |
| O1—C1—N1—C13 | 4.0 (5) | C4—N4—Mn—O5 | 85.6 (2) |
| C2—C1—N1—C13 | −174.9 (3) | C3—N4—Mn—N1 | 38.6 (3) |
| O1—C1—N1—Mn | −161.0 (2) | C4—N4—Mn—N1 | −163.2 (2) |
| C2—C1—N1—Mn | 20.1 (4) | C3—N4—Mn—N2 | 119.8 (3) |
| C12—C13—N1—C1 | 177.7 (3) | C4—N4—Mn—N2 | −82.0 (3) |
| C14—C13—N1—C1 | 61.2 (4) | C3—N4—Mn—N3 | 179.9 (3) |
| C15—C13—N1—C1 | −65.3 (4) | C4—N4—Mn—N3 | −21.9 (2) |
| C12—C13—N1—Mn | −15.9 (3) | C26—N5—C22—C23 | −175.3 (3) |
| C14—C13—N1—Mn | −132.3 (2) | C28—N5—C22—C23 | −53.9 (4) |
| C15—C13—N1—Mn | 101.1 (3) | C24—N5—C22—C23 | 63.8 (4) |
| O4—C12—N2—C11 | 9.9 (5) | C22—N5—C24—C25 | 62.8 (4) |
| C13—C12—N2—C11 | −169.4 (3) | C26—N5—C24—C25 | −55.2 (4) |
| O4—C12—N2—Mn | −171.8 (3) | C28—N5—C24—C25 | −176.6 (3) |
| C13—C12—N2—Mn | 9.0 (4) | C22—N5—C26—C27 | −175.1 (3) |
| C10—C11—N2—C12 | −15.6 (5) | C28—N5—C26—C27 | 64.0 (4) |
| C6—C11—N2—C12 | 162.5 (3) | C24—N5—C26—C27 | −54.2 (4) |
| C10—C11—N2—Mn | 166.0 (3) | C22—N5—C28—C29 | −55.0 (4) |
| C6—C11—N2—Mn | −15.9 (3) | C26—N5—C28—C29 | 63.1 (4) |
| O3—C5—N3—C6 | −3.8 (5) | C24—N5—C28—C29 | −175.7 (3) |
| C4—C5—N3—C6 | 178.2 (3) | | |

**Fig. 1**


C8
C7
O3
C9
C6
C10
C5
C20
N3
C11
C4
N2
O4
Mn
C12
C21
N4
C3
C19
N1
O2
O5
C14
C18
C13
C1
C2
C15
C16
O1
C17
C25
C27
C24
C26
N5
C22
C28
C23
C29