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# Crystal structure of bis(μ-2-benzoyl-benzoato-κ²*O*:*O*′)bis[bis(2,2′-bipyridine-κ²*N*,*N*′)manganese(II)] bis(perchlorate)

## Ibrahim Kani

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The title compound, $[Mn_2(C_6H_5COC_6H_4COO)_2(C_{10}H_8N_2)_4](ClO_4)_2$, comprises a centrosymmetric binuclear cation and two perchlorate anions. In the complex cation, two $Mn^{II}$ atoms are bridged by two O atoms of two different 2-benzoyl-benzoate ligands, each $Mn^{II}$ atom being further coordinated by two 2,2′-bipyridine (bipy) ligands in a distorted octahedral environment. Within the binuclear molecule, the Mn⋯Mn separation is 4.513 (7) Å. Intermolecular C—H⋯O and C—H⋯$\pi$ interactions link the molecules into a three-dimensional network.

## 1. Related literature

For applications of inorganic–organic complexes, see: Burd *et al.* (2012); FitzGerald *et al.* (2013); Huang *et al.* (2013); Carrington *et al.* (2014); Wu *et al.* (2005); Lee *et al.* (2009); Li *et al.* (2014); Zhou *et al.* (2013); Wang *et al.* (2014); Hagrman *et al.* (1999); Ghosh & Bharadwaj (2004); Evans *et al.* (1999); Maspoch *et al.* (2007); Kitagawa & Matsuda (2007). For manganese complexes with bipyridine, see: Lopes *et al.* (2011); Knight *et al.* (2010); McCann *et al.* (1998); Lumme & Lindell (1988); Li *et al.* (2002, 2011); Wang *et al.* (2012).
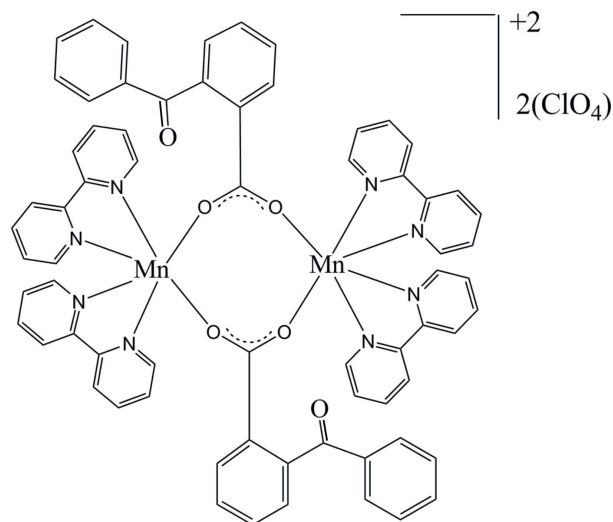


## 2. Experimental

### 2.1. Crystal data

$[Mn_2(C_{14}H_9O_3)_2(C_{10}H_8N_2)_4](ClO_4)_2$
$M_r = 1383.94$
Monoclinic, $P2_1/n$
$a = 13.348 (4)$ Å
$b = 17.136 (5)$ Å
$c = 14.499 (4)$ Å
$\beta = 111.321 (10)°$

$V = 3089.3 (16)$ Å$^3$
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.57$ mm$^{-1}$
$T = 296$ K
$0.27 \times 0.23 \times 0.12$ mm

### 2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.857$, $T_{max} = 0.935$

39502 measured reflections
7799 independent reflections
5603 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.130$
$S = 1.06$
6892 reflections

424 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.52$ e Å$^{-3}$
$\Delta\rho_{min} = -0.53$ e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Mn1—O2 | 2.0949 (16) | Mn1—N2 | 2.2281 (18) |
| Mn1—O1$^i$ | 2.1260 (14) | Mn1—N1 | 2.2555 (18) |
| Mn1—N3 | 2.2158 (17) | Mn1—N4 | 2.3037 (19) |

Symmetry code: (i) $-x + 1, -y, -z + 2$.

# data reports

## Table 2
Hydrogen-bond geometry (Å, °).

*Cg*7 is the centroid of the C22–C27 ring.

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C8—H8$\cdots$O5$^{ii}$ | 0.93 | 2.65 | 3.420 (4) | 141 |
| C26—H26$\cdots$O6$^{iii}$ | 0.93 | 2.58 | 3.494 (4) | 168 |
| C17—H17$\cdots$O4$^{iv}$ | 0.93 | 2.46 | 3.304 (4) | 152 |
| C18—H18$\cdots$O7$^{iv}$ | 0.93 | 2.72 | 3.382 (5) | 129 |
| C33—H33$\cdots$*Cg*7$^{iv}$ | 0.93 | 2.93 | 3.793 (3) | 146 |

Symmetry codes: (ii) $-x+1, -y, -z+1$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* ( Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

## Acknowledgements

## References

Bruker (2004). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burd, S. D., Ma, S., Perman, J. A., Sikora, B. J., Snurr, R. Q., Thallapally, P. K., Tian, J., Wojtas, L. & Zaworotko, M. J. (2012). *J. Am. Chem. Soc.* **134**, 3663–3666.

Carrington, E. J., Vitórica-Yrezábal, I. J. & Brammer, L. (2014). *Acta Cryst.* B**70**, 404–422.

Evans, O. R., Xiong, R., Wang, Z., Wong, G. K. & Lin, W. (1999). *Angew. Chem.* **111**, 557–559.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

FitzGerald, S. A., Pierce, C. J., Rowsell, J. L. C., Bloch, E. D. & Mason, J. A. (2013). *J. Am. Chem. Soc.* **135**, 9458–9464.

Ghosh, S. K. & Bharadwaj, P. K. (2004). *Inorg. Chem.* **43**, 2293–2298.

Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.

Huang, Y.-L., Gong, Y.-N., Jiang, L. & Lu, T.-B. (2013). *Chem. Commun.* **49**, 1753–1755.

Kitagawa, S. & Matsuda, R. (2007). *Coord. Chem. Rev.* **251**, 2490–2509.

Knight, J. C., Amoroso, A. J., Edwards, P. G., Prabaharan, R. & Singh, N. (2010). *Dalton Trans.* **39**, 8925–8936.

Lee, J., Farha, O. K., Roberts, J., Scheidt, K. A., Nguyen, S. T. & Hupp, J. T. (2009). *Chem. Soc. Rev.* **38**, 1450–1459.

Li, L., Matsuda, R., Tanaka, I., Sato, H., Kanoo, P., Jeon, H. J., Foo, M. L., Wakamiya, A., Murata, Y. & Kitagawa, S. (2014). *J. Am. Chem. Soc.* **136**, 7543–7546.

Li, Z. Y., Xu, D. J., Nie, J. J., Wu, Z. Y., Wu, J. Y. & Chiang, M. (2002). *J. Coord. Chem.* **55**, 1155–1160.

Li, K., Zhang, C. & Xu, W. (2011). *Acta Cryst.* E**67**, m1443–m1444.

Lopes, L. B., Corrêa, C. C. & Diniz, R. (2011). *Acta Cryst.* E**67**, m906–m907.

Lumme, P. O. & Lindell, E. (1988). *Acta Cryst.* C**44**, 463–465.

Maspoch, D., Ruiz-Molina, D. & Veciana, J. (2007). *Chem. Soc. Rev.* **36**, 770–818.

McCann, S., McCann, M., Casey, M. T., Jackman, M., Devereux, M. & McKee, V. (1998). *Inorg. Chim. Acta*, **279**, 24–29.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Wang, C., Liu, D., Xie, Z. & Lin, W. (2014). *Inorg. Chem.* **53**, 1331–1338.

Wang, H., Wang, S. & Lang, Y. (2012). *Acta Cryst.* E**68**, m569.

Wu, C.-D., Hu, A., Zhang, L. & Lin, W. (2005). *J. Am. Chem. Soc.* **127**, 8940–8941.

Zhou, J.-M., Shi, W., Xu, N. & Cheng, P. (2013). *Inorg. Chem.* **52**, 8082–8090.

# supporting information

## Crystal structure of bis(*μ*-2-benzoylbenzoato-*κ²O:O′*)bis[bis(2,2′-bipyridine-*κ²N,N′*)manganese(II)] bis(perchlorate)

### Ibrahim Kani

### S1. Chemical context

The design of inorganic-organic supramolecular complexes is of current interest in the fields of supramolecular chemistry and crystal engineering. This interest stems from their potential applications as functional materials, such as in gas storage, separation (Burd *et al.*, 2012; FitzGerald *et al.*, 2013; Huang *et al.*, 2013; Carrington *et al.*, 2014), catalysis (Wu *et al.*, 2005; Lee *et al.*, 2009; Li *et al.*, 2014), luminesans, optic, magnetism (Maspoch *et al.*, 2007, Kitagawa &Matsuda 2007, Zhou *et al.*, 2013; Wang *et al.*, 2014), and their further potential medical value derived from their antiviral and the inhibition of angiogenesis (Hagrman *et al.*, 1999; Ghosh *et al.*, 2004; Evans *et al.*, 1999).

### S2. Structural commentary

In this paper, we will report the synthesis and structure of a new bimetallic manganese complex, [Mn$_2$(C$_6$H$_5$COC$_6$H$_4$COO)$_2$(C$_{10}$H$_8$N$_2$)$_4$](ClO$_4$)$_2$]. The molecular structure of the complex is illustrated in Fig.1. In the centrosymmetric binuclear molecule the Mn(II) ion is coordinated by two O atoms from two different benzoyl benzoate ligands, four N atoms from two chelating bipy ligands, generating a distorted octahedral MnN4O2 coordination geometry. The *cisoid* bond angles fall in the region 72.8 (7)–101.5 (7)°, and *transoid* ones are 161.5 (7)°, and 172.9 (7)° exhibiting substantial deviations from an ideal octahedral geometry.

The Mn–O bond lentghs are 2.095 (2) Å and 2.126 (1) Å (Supplementary Table) The mean Mn—N(bipy) distance of 2.251 (2) Å and the bite angles N1—Mn1—N2 of 73.1 (7)° and N3—Mn1—N3 of 72.8 (4)° are close to the corresponding values observed in related manganese-bipy complexes (Lopes *et al.*, 2011; Knight *et al.*, 2010; McCann *et al.*, 1998; Lumme & Lindell, 1988; Li *et al.*, 2002, 2011; Wang *et al.*, 2012). The dihedral angles between the rings of bipy ligands are −3.8 (3) ° (ligand containing N3 and N4) and −5.6 (3)° (ligand containing N1 and N2).

### S3. Supramolecular features

In the crystal structure binuclear species are assembled into a three-dimensional supramolecular architecture by O—H···O, C—H···C hydrogen bonds and C—H··· *π*, and *π*–*π* interactions (Fig. 2, Table 2). The closest centroid-centroid distance of the N1,C1—C5 rings is 4.031 Å. The complex molecules are weakly linked by hydrogen bonds through the perchlorate ions to generate the three-dimensional supramolecular structure.

### S4. Synthesis and crystallization

Mn(ClO$_4$)$_2$·6H$_2$O in methanol (0.076 mmol) was added slowly to a mixed solution of 2,2?-bipyridine (0.155 mmol) and benzoyl benzoic acid (0.080 mmol) in methanol (7 ml). After refluxing for 3 h, the mixture was filtered off while hot. The green color single crystals suitable for X-ray analysis were obtained by slow evaporation of the above filtrate at room temperature after a week.

## S5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.
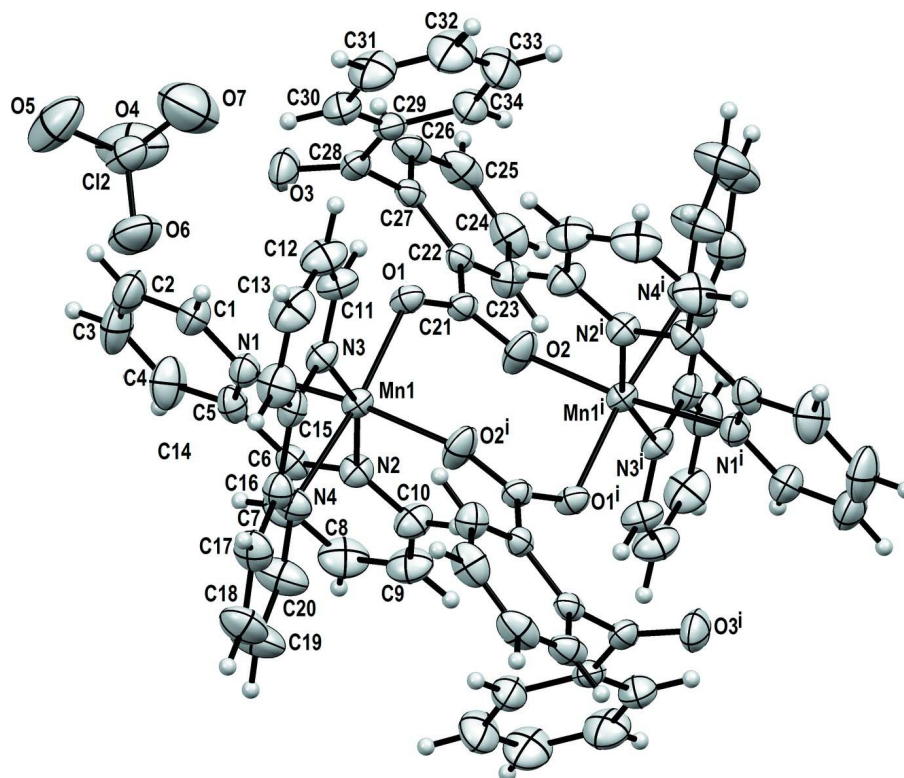


**Figure 1**

The molecular structure of the title compound, (displacement ellipsoids are shown at 50% probability levels). Symmetry code: (i) $-x + 1$, $-y$, $-z + 2$.
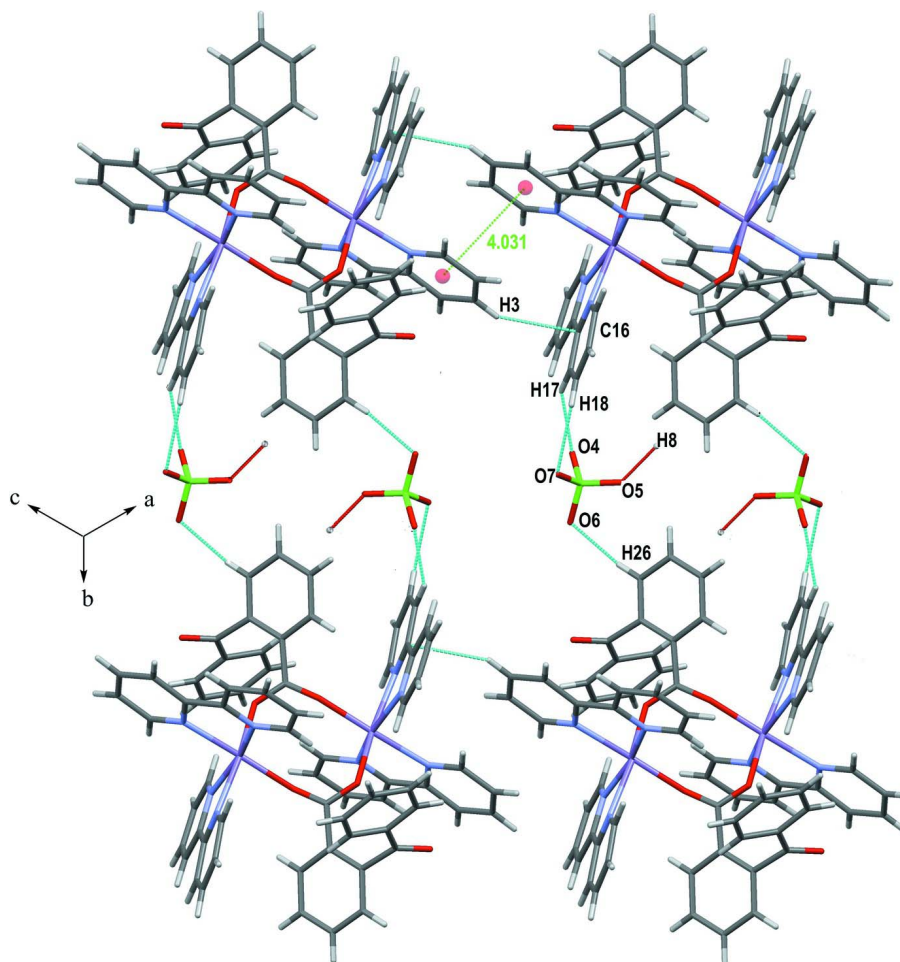
**Figure 2**

Packing view drawn along the *c* axis, showing O—H···O, C—H···C hydrogen bonds and C—H··· *π*, and *π*–*π* stacking interactions drawn as dotted lines.

**Bis(*μ*-2-benzoylbenzoato-*κ²O:O′*)bis[bis(2,2′-bipyridine-*κ²N,N′*)manganese(II)] bis(perchlorate)**

*Crystal data*

| | |
|---|---|
| $[Mn_2(C_{14}H_9O_3)_2(C_{10}H_8N_2)_4](ClO_4)_2$ | $F(000) = 1420$ |
| $M_r = 1383.94$ | $D_x = 1.488$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 13.348$ (4) Å | Cell parameters from 8617 reflections |
| $b = 17.136$ (5) Å | $\theta = 2.5$–$28.2°$ |
| $c = 14.499$ (4) Å | $\mu = 0.57$ mm$^{-1}$ |
| $\beta = 111.321$ (10)° | $T = 296$ K |
| $V = 3089.3$ (16) Å$^3$ | Square, yellow |
| $Z = 2$ | $0.27 \times 0.23 \times 0.12$ mm |

*Data collection*

| | |
|---|---|
| Bruker APEXII CCD diffractometer | phi and $\omega$ scans |
| Radiation source: fine-focus sealed tube | Absorption correction: multi-scan (*SADABS*; Bruker, 2004) |
| Graphite monochromator | $T_{min} = 0.857$, $T_{max} = 0.935$ |

39502 measured reflections
7799 independent reflections
5603 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$

$\theta_{max} = 28.5°$, $\theta_{min} = 1.8°$
$h = -16 \rightarrow 17$
$k = -22 \rightarrow 19$
$l = -19 \rightarrow 19$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.130$
$S = 1.06$
6892 reflections
424 parameters
0 restraints
Primary atom site location: structure-invariant
   direct methods

Secondary atom site location: difference Fourier
   map
Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.073P)^2 + 1.2301P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.52$ e Å$^{-3}$
$\Delta\rho_{min} = -0.53$ e Å$^{-3}$

*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 $F^2 > \sigma(F^2)$ 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 (Å²)*

|     | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ |
| --- | --- | --- | --- | --- |
| Mn1 | 0.33958 (2) | 0.022476 (15) | 1.01401 (2) | 0.03203 (11) |
| C29 | 0.54535 (17) | 0.19533 (12) | 0.76826 (15) | 0.0413 (5) |
| Cl2 | 0.81581 (7) | 0.02743 (3) | 0.63743 (5) | 0.0627 (2) |
| O1 | 0.58328 (12) | 0.08588 (7) | 0.93327 (10) | 0.0384 (3) |
| O3 | 0.72438 (13) | 0.22041 (12) | 0.87465 (14) | 0.0610 (5) |
| O2 | 0.47457 (14) | 0.08637 (9) | 1.01711 (15) | 0.0590 (5) |
| O6 | 0.8226 (2) | −0.04173 (14) | 0.6922 (2) | 0.0967 (8) |
| O5 | 0.8838 (3) | 0.02323 (14) | 0.5845 (3) | 0.1155 (11) |
| O4 | 0.8379 (3) | 0.09348 (15) | 0.69834 (19) | 0.1176 (11) |
| N1 | 0.18370 (14) | −0.03974 (10) | 0.99225 (14) | 0.0414 (4) |
| N2 | 0.27238 (15) | −0.01610 (10) | 0.85656 (13) | 0.0398 (4) |
| N3 | 0.35547 (14) | 0.07990 (10) | 1.15558 (13) | 0.0400 (4) |
| N4 | 0.24957 (16) | 0.13976 (10) | 0.97526 (14) | 0.0472 (4) |
| O7 | 0.7095 (3) | 0.0362 (2) | 0.5656 (3) | 0.1379 (13) |
| C5 | 0.13050 (17) | −0.06874 (12) | 0.90196 (17) | 0.0437 (5) |
| C4 | 0.0383 (2) | −0.11325 (18) | 0.8835 (3) | 0.0711 (8) |
| H4 | 0.0008 | −0.1328 | 0.8205 | 0.085* |
| C3 | 0.0035 (2) | −0.1279 (2) | 0.9606 (3) | 0.0837 (10) |
| H3 | −0.0576 | −0.1581 | 0.9499 | 0.100* |
| C2 | 0.0580 (2) | −0.09852 (18) | 1.0515 (3) | 0.0691 (8) |
| H2 | 0.0354 | −0.1081 | 1.1039 | 0.083* |

| C1 | 0.1471 (2) | −0.05439 (15) | 1.0643 (2) | 0.0532 (6) |
| H1 | 0.1841 | −0.0335 | 1.1267 | 0.064* |
| C6 | 0.17701 (17) | −0.05233 (12) | 0.82610 (16) | 0.0421 (5) |
| C10 | 0.3191 (2) | −0.00160 (14) | 0.79121 (17) | 0.0498 (5) |
| H10 | 0.3855 | 0.0235 | 0.8131 | 0.060* |
| C9 | 0.2740 (3) | −0.02187 (15) | 0.69354 (18) | 0.0609 (7) |
| H9 | 0.3091 | −0.0116 | 0.6499 | 0.073* |
| C8 | 0.1752 (3) | −0.05798 (18) | 0.6619 (2) | 0.0698 (8) |
| H8 | 0.1417 | −0.0719 | 0.5957 | 0.084* |
| C7 | 0.1266 (2) | −0.07322 (16) | 0.72797 (19) | 0.0632 (7) |
| H7 | 0.0598 | −0.0976 | 0.7071 | 0.076* |
| C21 | 0.53450 (15) | 0.11944 (10) | 0.98092 (14) | 0.0343 (4) |
| C22 | 0.55033 (15) | 0.20527 (10) | 0.99784 (14) | 0.0332 (4) |
| C27 | 0.59429 (15) | 0.25089 (10) | 0.94292 (14) | 0.0345 (4) |
| C28 | 0.62929 (17) | 0.21976 (11) | 0.86348 (16) | 0.0405 (5) |
| C30 | 0.5765 (2) | 0.15888 (15) | 0.69870 (18) | 0.0555 (6) |
| H30 | 0.6490 | 0.1492 | 0.7118 | 0.067* |
| C31 | 0.5003 (3) | 0.1367 (2) | 0.6095 (2) | 0.0731 (8) |
| H31 | 0.5215 | 0.1117 | 0.5627 | 0.088* |
| C32 | 0.3929 (3) | 0.1511 (2) | 0.5893 (2) | 0.0808 (9) |
| H32 | 0.3419 | 0.1354 | 0.5291 | 0.097* |
| C33 | 0.3611 (2) | 0.1883 (2) | 0.6571 (2) | 0.0726 (8) |
| H33 | 0.2887 | 0.1993 | 0.6426 | 0.087* |
| C34 | 0.4369 (2) | 0.20974 (15) | 0.74772 (17) | 0.0528 (6) |
| H34 | 0.4152 | 0.2338 | 0.7949 | 0.063* |
| C26 | 0.60483 (18) | 0.33052 (12) | 0.96073 (18) | 0.0482 (5) |
| H26 | 0.6345 | 0.3616 | 0.9246 | 0.058* |
| C25 | 0.5722 (2) | 0.36409 (12) | 1.0307 (2) | 0.0574 (7) |
| H25 | 0.5779 | 0.4178 | 1.0403 | 0.069* |
| C24 | 0.5313 (2) | 0.31917 (14) | 1.0867 (2) | 0.0575 (6) |
| H24 | 0.5107 | 0.3418 | 1.1353 | 0.069* |
| C23 | 0.52106 (18) | 0.23995 (13) | 1.07001 (17) | 0.0458 (5) |
| H23 | 0.4938 | 0.2092 | 1.1083 | 0.055* |
| C15 | 0.32092 (17) | 0.15410 (12) | 1.15152 (16) | 0.0414 (5) |
| C16 | 0.26552 (17) | 0.18769 (12) | 1.05165 (17) | 0.0429 (5) |
| C20 | 0.2014 (3) | 0.16810 (16) | 0.8851 (2) | 0.0727 (8) |
| H20 | 0.1894 | 0.1346 | 0.8317 | 0.087* |
| C19 | 0.1679 (3) | 0.24425 (19) | 0.8656 (2) | 0.0846 (10) |
| H19 | 0.1345 | 0.2619 | 0.8009 | 0.102* |
| C18 | 0.1850 (3) | 0.29259 (16) | 0.9434 (2) | 0.0740 (8) |
| H18 | 0.1639 | 0.3446 | 0.9329 | 0.089* |
| C17 | 0.2335 (2) | 0.26480 (14) | 1.0375 (2) | 0.0582 (6) |
| H17 | 0.2447 | 0.2975 | 1.0916 | 0.070* |
| C14 | 0.3385 (2) | 0.19644 (15) | 1.23753 (19) | 0.0583 (6) |
| H14 | 0.3142 | 0.2476 | 1.2344 | 0.070* |
| C13 | 0.3920 (3) | 0.16196 (18) | 1.3268 (2) | 0.0692 (8) |
| H13 | 0.4037 | 0.1895 | 1.3850 | 0.083* |
| C12 | 0.4285 (3) | 0.08675 (17) | 1.33073 (19) | 0.0643 (7) |

| | | | |
|---|---|---|---|
| H12 | 0.4660 | 0.0627 | 1.3910 | 0.077* |
| C11 | 0.4078 (2) | 0.04829 (14) | 1.24293 (17) | 0.0519 (5) |
| H11 | 0.4319 | −0.0028 | 1.2450 | 0.062* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Mn1 | 0.0380 (2) | 0.02841 (15) | 0.03140 (17) | −0.00411 (10) | 0.01470 (14) | −0.00338 (10) |
| C29 | 0.0429 (12) | 0.0437 (10) | 0.0358 (10) | −0.0035 (9) | 0.0128 (9) | 0.0106 (8) |
| Cl2 | 0.0910 (5) | 0.0447 (3) | 0.0708 (4) | 0.0073 (3) | 0.0514 (4) | 0.0037 (3) |
| O1 | 0.0505 (8) | 0.0298 (6) | 0.0389 (7) | −0.0006 (5) | 0.0210 (7) | 0.0029 (5) |
| O3 | 0.0359 (9) | 0.0848 (12) | 0.0638 (11) | −0.0114 (8) | 0.0201 (8) | 0.0015 (9) |
| O2 | 0.0678 (11) | 0.0397 (8) | 0.0887 (13) | −0.0165 (7) | 0.0512 (10) | −0.0046 (8) |
| O6 | 0.128 (2) | 0.0668 (13) | 0.115 (2) | 0.0097 (13) | 0.0686 (18) | 0.0332 (13) |
| O5 | 0.175 (3) | 0.0781 (16) | 0.152 (3) | −0.0089 (16) | 0.129 (2) | −0.0082 (15) |
| O4 | 0.210 (3) | 0.0697 (14) | 0.0783 (16) | 0.0250 (18) | 0.0579 (19) | −0.0091 (12) |
| N1 | 0.0359 (9) | 0.0427 (9) | 0.0473 (10) | −0.0031 (7) | 0.0169 (8) | 0.0002 (7) |
| N2 | 0.0420 (10) | 0.0413 (9) | 0.0346 (9) | −0.0044 (7) | 0.0120 (8) | −0.0055 (7) |
| N3 | 0.0481 (10) | 0.0393 (8) | 0.0378 (9) | −0.0056 (7) | 0.0218 (8) | −0.0049 (7) |
| N4 | 0.0536 (11) | 0.0409 (9) | 0.0429 (10) | 0.0056 (8) | 0.0126 (9) | −0.0018 (7) |
| O7 | 0.120 (3) | 0.123 (3) | 0.142 (3) | 0.0136 (19) | 0.013 (2) | 0.034 (2) |
| C5 | 0.0329 (11) | 0.0396 (10) | 0.0555 (13) | −0.0022 (8) | 0.0125 (10) | −0.0052 (9) |
| C4 | 0.0506 (16) | 0.0759 (18) | 0.086 (2) | −0.0242 (13) | 0.0244 (15) | −0.0266 (16) |
| C3 | 0.0553 (17) | 0.087 (2) | 0.122 (3) | −0.0286 (16) | 0.0489 (19) | −0.017 (2) |
| C2 | 0.0595 (17) | 0.0725 (17) | 0.090 (2) | −0.0093 (14) | 0.0452 (16) | 0.0057 (16) |
| C1 | 0.0487 (14) | 0.0593 (13) | 0.0579 (14) | −0.0031 (11) | 0.0270 (12) | 0.0045 (11) |
| C6 | 0.0390 (12) | 0.0381 (9) | 0.0424 (11) | 0.0001 (8) | 0.0070 (9) | −0.0054 (8) |
| C10 | 0.0581 (15) | 0.0540 (12) | 0.0395 (12) | −0.0075 (11) | 0.0201 (11) | −0.0048 (10) |
| C9 | 0.085 (2) | 0.0630 (15) | 0.0367 (12) | 0.0011 (13) | 0.0250 (13) | −0.0026 (10) |
| C8 | 0.085 (2) | 0.0727 (17) | 0.0381 (13) | −0.0082 (15) | 0.0055 (14) | −0.0109 (12) |
| C7 | 0.0603 (17) | 0.0682 (16) | 0.0460 (14) | −0.0132 (13) | 0.0015 (12) | −0.0122 (12) |
| C21 | 0.0346 (10) | 0.0295 (8) | 0.0374 (10) | −0.0036 (7) | 0.0114 (8) | 0.0032 (7) |
| C22 | 0.0283 (10) | 0.0300 (8) | 0.0379 (10) | −0.0024 (7) | 0.0079 (8) | 0.0013 (7) |
| C27 | 0.0266 (10) | 0.0309 (8) | 0.0380 (10) | −0.0040 (7) | 0.0021 (8) | 0.0051 (7) |
| C28 | 0.0374 (12) | 0.0392 (10) | 0.0447 (11) | −0.0051 (8) | 0.0148 (9) | 0.0096 (8) |
| C30 | 0.0577 (15) | 0.0670 (15) | 0.0441 (13) | 0.0021 (12) | 0.0212 (12) | 0.0096 (11) |
| C31 | 0.087 (2) | 0.092 (2) | 0.0400 (14) | −0.0023 (17) | 0.0229 (14) | −0.0025 (13) |
| C32 | 0.076 (2) | 0.115 (3) | 0.0374 (14) | −0.0142 (19) | 0.0036 (14) | −0.0023 (15) |
| C33 | 0.0487 (16) | 0.108 (2) | 0.0479 (15) | −0.0024 (15) | 0.0013 (13) | 0.0014 (15) |
| C34 | 0.0447 (14) | 0.0673 (14) | 0.0421 (12) | −0.0022 (11) | 0.0107 (11) | 0.0028 (10) |
| C26 | 0.0432 (13) | 0.0321 (9) | 0.0561 (13) | −0.0058 (8) | 0.0024 (11) | 0.0081 (9) |
| C25 | 0.0527 (14) | 0.0301 (9) | 0.0729 (17) | −0.0001 (9) | 0.0031 (13) | −0.0062 (10) |
| C24 | 0.0546 (15) | 0.0498 (12) | 0.0620 (15) | 0.0069 (11) | 0.0140 (13) | −0.0188 (11) |
| C23 | 0.0443 (12) | 0.0448 (11) | 0.0495 (12) | −0.0028 (9) | 0.0185 (10) | −0.0051 (9) |
| C15 | 0.0415 (12) | 0.0402 (10) | 0.0489 (12) | −0.0055 (8) | 0.0240 (10) | −0.0084 (8) |
| C16 | 0.0404 (12) | 0.0387 (10) | 0.0523 (12) | −0.0016 (8) | 0.0202 (10) | −0.0053 (9) |
| C20 | 0.094 (2) | 0.0569 (15) | 0.0504 (15) | 0.0180 (14) | 0.0065 (15) | 0.0008 (12) |
| C19 | 0.103 (3) | 0.0684 (18) | 0.0653 (19) | 0.0278 (17) | 0.0095 (18) | 0.0171 (15) |

| C18 | 0.084 (2) | 0.0457 (13) | 0.084 (2) | 0.0187 (13) | 0.0202 (17) | 0.0108 (13) |
|---|---|---|---|---|---|---|
| C17 | 0.0617 (16) | 0.0423 (11) | 0.0729 (17) | 0.0050 (10) | 0.0272 (14) | −0.0063 (11) |
| C14 | 0.0686 (17) | 0.0554 (13) | 0.0563 (15) | 0.0002 (12) | 0.0292 (13) | −0.0174 (11) |
| C13 | 0.089 (2) | 0.0789 (18) | 0.0464 (14) | −0.0084 (15) | 0.0320 (14) | −0.0218 (13) |
| C12 | 0.083 (2) | 0.0711 (17) | 0.0387 (13) | −0.0101 (14) | 0.0221 (13) | −0.0029 (11) |
| C11 | 0.0677 (16) | 0.0490 (11) | 0.0409 (12) | −0.0048 (11) | 0.0221 (11) | 0.0031 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Mn1—O2 | 2.0949 (16) | C8—H8 | 0.9300 |
| Mn1—O1$^{i}$ | 2.1260 (14) | C7—H7 | 0.9300 |
| Mn1—N3 | 2.2158 (17) | C21—C22 | 1.493 (2) |
| Mn1—N2 | 2.2281 (18) | C22—C23 | 1.378 (3) |
| Mn1—N1 | 2.2555 (18) | C22—C27 | 1.389 (3) |
| Mn1—N4 | 2.3037 (19) | C27—C26 | 1.386 (3) |
| C29—C30 | 1.373 (3) | C27—C28 | 1.490 (3) |
| C29—C34 | 1.390 (3) | C30—C31 | 1.377 (4) |
| C29—C28 | 1.487 (3) | C30—H30 | 0.9300 |
| Cl2—O5 | 1.386 (3) | C31—C32 | 1.377 (5) |
| Cl2—O4 | 1.400 (3) | C31—H31 | 0.9300 |
| Cl2—O6 | 1.411 (2) | C32—C33 | 1.364 (5) |
| Cl2—O7 | 1.430 (3) | C32—H32 | 0.9300 |
| O1—C21 | 1.249 (2) | C33—C34 | 1.385 (4) |
| O1—Mn1$^{i}$ | 2.1260 (14) | C33—H33 | 0.9300 |
| O3—C28 | 1.220 (3) | C34—H34 | 0.9300 |
| O2—C21 | 1.242 (2) | C26—C25 | 1.368 (4) |
| N1—C1 | 1.329 (3) | C26—H26 | 0.9300 |
| N1—C5 | 1.338 (3) | C25—C24 | 1.368 (4) |
| N2—C10 | 1.334 (3) | C25—H25 | 0.9300 |
| N2—C6 | 1.339 (3) | C24—C23 | 1.377 (3) |
| N3—C11 | 1.320 (3) | C24—H24 | 0.9300 |
| N3—C15 | 1.346 (3) | C23—H23 | 0.9300 |
| N4—C20 | 1.322 (3) | C15—C14 | 1.387 (3) |
| N4—C16 | 1.332 (3) | C15—C16 | 1.482 (3) |
| C5—C4 | 1.388 (3) | C16—C17 | 1.381 (3) |
| C5—C6 | 1.473 (3) | C20—C19 | 1.375 (4) |
| C4—C3 | 1.381 (5) | C20—H20 | 0.9300 |
| C4—H4 | 0.9300 | C19—C18 | 1.351 (5) |
| C3—C2 | 1.349 (5) | C19—H19 | 0.9300 |
| C3—H3 | 0.9300 | C18—C17 | 1.366 (4) |
| C2—C1 | 1.363 (4) | C18—H18 | 0.9300 |
| C2—H2 | 0.9300 | C17—H17 | 0.9300 |
| C1—H1 | 0.9300 | C14—C13 | 1.364 (4) |
| C6—C7 | 1.382 (3) | C14—H14 | 0.9300 |
| C10—C9 | 1.367 (3) | C13—C12 | 1.371 (4) |
| C10—H10 | 0.9300 | C13—H13 | 0.9300 |
| C9—C8 | 1.376 (4) | C12—C11 | 1.370 (3) |
| C9—H9 | 0.9300 | C12—H12 | 0.9300 |

| | | | |
|---|---|---|---|
| C8—C7 | 1.364 (4) | C11—H11 | 0.9300 |
| | | | |
| O2—Mn1—O1<sup>i</sup> | 98.53 (7) | O2—C21—C22 | 117.04 (18) |
| O2—Mn1—N3 | 87.49 (7) | O1—C21—C22 | 118.25 (16) |
| O1<sup>i</sup>—Mn1—N3 | 100.61 (6) | C23—C22—C27 | 119.23 (18) |
| O2—Mn1—N2 | 101.52 (7) | C23—C22—C21 | 119.16 (18) |
| O1<sup>i</sup>—Mn1—N2 | 94.08 (6) | C27—C22—C21 | 121.61 (18) |
| N3—Mn1—N2 | 161.48 (7) | C26—C27—C22 | 118.8 (2) |
| O2—Mn1—N1 | 172.97 (7) | C26—C27—C28 | 117.20 (19) |
| O1<sup>i</sup>—Mn1—N1 | 86.51 (6) | C22—C27—C28 | 123.93 (16) |
| N3—Mn1—N1 | 96.45 (7) | O3—C28—C29 | 121.5 (2) |
| N2—Mn1—N1 | 73.10 (7) | O3—C28—C27 | 119.8 (2) |
| O2—Mn1—N4 | 85.27 (7) | C29—C28—C27 | 118.44 (18) |
| O1<sup>i</sup>—Mn1—N4 | 172.33 (6) | C29—C30—C31 | 119.9 (3) |
| N3—Mn1—N4 | 72.80 (7) | C29—C30—H30 | 120.1 |
| N2—Mn1—N4 | 91.66 (7) | C31—C30—H30 | 120.1 |
| N1—Mn1—N4 | 90.31 (7) | C30—C31—C32 | 120.5 (3) |
| C30—C29—C34 | 119.6 (2) | C30—C31—H31 | 119.8 |
| C30—C29—C28 | 118.9 (2) | C32—C31—H31 | 119.8 |
| C34—C29—C28 | 121.6 (2) | C33—C32—C31 | 120.2 (3) |
| O5—Cl2—O4 | 111.14 (19) | C33—C32—H32 | 119.9 |
| O5—Cl2—O6 | 110.27 (16) | C31—C32—H32 | 119.9 |
| O4—Cl2—O6 | 111.62 (18) | C32—C33—C34 | 119.8 (3) |
| O5—Cl2—O7 | 106.2 (2) | C32—C33—H33 | 120.1 |
| O4—Cl2—O7 | 107.5 (2) | C34—C33—H33 | 120.1 |
| O6—Cl2—O7 | 110.0 (2) | C33—C34—C29 | 120.1 (2) |
| C21—O1—Mn1<sup>i</sup> | 119.02 (12) | C33—C34—H34 | 120.0 |
| C21—O2—Mn1 | 155.61 (17) | C29—C34—H34 | 120.0 |
| C1—N1—C5 | 118.9 (2) | C25—C26—C27 | 120.9 (2) |
| C1—N1—Mn1 | 124.31 (16) | C25—C26—H26 | 119.5 |
| C5—N1—Mn1 | 116.55 (14) | C27—C26—H26 | 119.5 |
| C10—N2—C6 | 119.11 (19) | C24—C25—C26 | 120.4 (2) |
| C10—N2—Mn1 | 123.68 (15) | C24—C25—H25 | 119.8 |
| C6—N2—Mn1 | 117.12 (14) | C26—C25—H25 | 119.8 |
| C11—N3—C15 | 118.87 (19) | C25—C24—C23 | 119.1 (2) |
| C11—N3—Mn1 | 123.07 (15) | C25—C24—H24 | 120.4 |
| C15—N3—Mn1 | 117.58 (14) | C23—C24—H24 | 120.4 |
| C20—N4—C16 | 118.0 (2) | C24—C23—C22 | 121.4 (2) |
| C20—N4—Mn1 | 125.78 (17) | C24—C23—H23 | 119.3 |
| C16—N4—Mn1 | 115.06 (14) | C22—C23—H23 | 119.3 |
| N1—C5—C4 | 120.7 (2) | N3—C15—C14 | 120.8 (2) |
| N1—C5—C6 | 116.23 (18) | N3—C15—C16 | 116.79 (18) |
| C4—C5—C6 | 123.0 (2) | C14—C15—C16 | 122.4 (2) |
| C3—C4—C5 | 118.6 (3) | N4—C16—C17 | 121.3 (2) |
| C3—C4—H4 | 120.7 | N4—C16—C15 | 116.42 (18) |
| C5—C4—H4 | 120.7 | C17—C16—C15 | 122.3 (2) |
| C2—C3—C4 | 120.1 (3) | N4—C20—C19 | 123.8 (3) |
| C2—C3—H3 | 119.9 | N4—C20—H20 | 118.1 |

| | | | |
|---|---|---|---|
| C4—C3—H3 | 119.9 | C19—C20—H20 | 118.1 |
| C3—C2—C1 | 118.3 (3) | C18—C19—C20 | 117.8 (3) |
| C3—C2—H2 | 120.8 | C18—C19—H19 | 121.1 |
| C1—C2—H2 | 120.8 | C20—C19—H19 | 121.1 |
| N1—C1—C2 | 123.3 (3) | C19—C18—C17 | 119.7 (2) |
| N1—C1—H1 | 118.4 | C19—C18—H18 | 120.1 |
| C2—C1—H1 | 118.4 | C17—C18—H18 | 120.1 |
| N2—C6—C7 | 120.6 (2) | C18—C17—C16 | 119.3 (2) |
| N2—C6—C5 | 116.77 (19) | C18—C17—H17 | 120.3 |
| C7—C6—C5 | 122.7 (2) | C16—C17—H17 | 120.3 |
| N2—C10—C9 | 123.0 (2) | C13—C14—C15 | 119.0 (2) |
| N2—C10—H10 | 118.5 | C13—C14—H14 | 120.5 |
| C9—C10—H10 | 118.5 | C15—C14—H14 | 120.5 |
| C10—C9—C8 | 117.9 (3) | C14—C13—C12 | 120.1 (2) |
| C10—C9—H9 | 121.1 | C14—C13—H13 | 119.9 |
| C8—C9—H9 | 121.1 | C12—C13—H13 | 119.9 |
| C7—C8—C9 | 119.7 (2) | C11—C12—C13 | 117.7 (3) |
| C7—C8—H8 | 120.2 | C11—C12—H12 | 121.2 |
| C9—C8—H8 | 120.2 | C13—C12—H12 | 121.2 |
| C8—C7—C6 | 119.7 (3) | N3—C11—C12 | 123.5 (2) |
| C8—C7—H7 | 120.1 | N3—C11—H11 | 118.2 |
| C6—C7—H7 | 120.1 | C12—C11—H11 | 118.2 |
| O2—C21—O1 | 124.70 (17) | | |

Symmetry code: (i) −*x*+1, −*y*, −*z*+2.

*Hydrogen-bond geometry (Å, º)*

Cg7 is the centroid of the C22–C27 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C8—H8···O5ⁱⁱ | 0.93 | 2.65 | 3.420 (4) | 141 |
| C26—H26···O6ⁱⁱⁱ | 0.93 | 2.58 | 3.494 (4) | 168 |
| C17—H17···O4ⁱᵛ | 0.93 | 2.46 | 3.304 (4) | 152 |
| C18—H18···O7ⁱᵛ | 0.93 | 2.72 | 3.382 (5) | 129 |
| C33—H33···*Cg*7ⁱᵛ | 0.93 | 2.93 | 3.793 (3) | 146 |

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+3/2, *y*+1/2, −*z*+3/2; (iv) *x*−1/2, −*y*+1/2, *z*+1/2.