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# Synthesis, crystal structure and photophysical properties of a dinuclear $Mn^{II}$ complex with 6-(diethylamino)-4-phenyl-2-(pyridin-2-yl)quinoline

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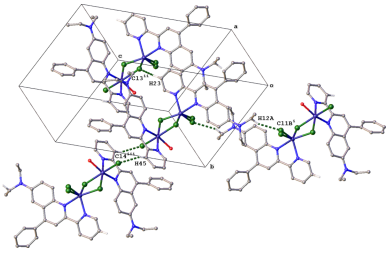
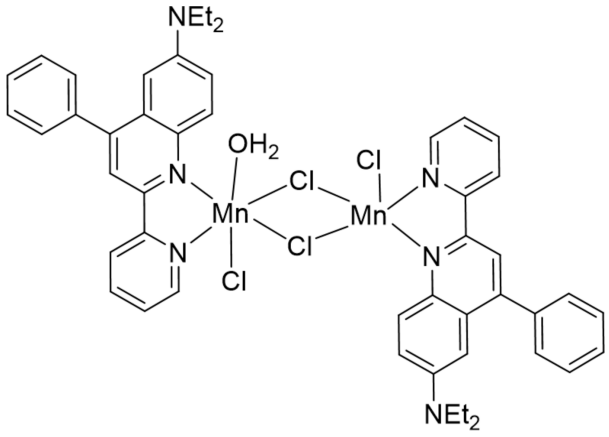
A new quinoline derivative, namely, 6-(diethylamino)-4-phenyl-2-(pyridin-2-yl)-quinoline, $C_{24}H_{23}N_3$ (**QP**), and its $Mn^{II}$ complex aqua-1$\kappa O$-di-$\mu$-chlorido-1:2$\kappa^4 Cl$:$Cl$-dichlorido-1$\kappa Cl$,2$\kappa Cl$-bis[6-(diethylamino)-4-phenyl-2-(pyridin-2-yl)-quinoline]-1$\kappa^2 N^1$,$N^2$;2$\kappa^2 N^1$,$N^2$-dimanganese(II), $[Mn_2Cl_4(C_{24}H_{23}N_3)_2(H_2O)]$ (**MnQP**), were synthesized. Their compositions have been determined with ESI-MS, IR, and $^1$H NMR spectroscopy. The crystal-structure determination of **MnQP** revealed a dinuclear complex with a central four-membered $Mn_2Cl_2$ ring. Both $Mn^{II}$ atoms bind to an additional Cl atom and to two N atoms of the **QP** ligand. One $Mn^{II}$ atom expands its coordination sphere with an extra water molecule, resulting in a distorted octahedral shape. The second $Mn^{II}$ atom shows a distorted trigonal–bipyramidal shape. The UV–vis absorption and emission spectra of the examined compounds were studied. Furthermore, when investigating the aggregation-induced emission (AIE) properties, it was found that the fluorescent color changes from blue to green and eventually becomes yellow as the fraction of water in the THF/water mixture increases from 0% to 99%. In particular, these color and intensity changes are most pronounced at a water fraction of 60%. The crystal structure contains disordered solvent molecules, which could not be modeled. The SQUEEZE procedure [Spek (2015). *Acta Cryst.* C**71**, 9–18] was used to obtain information on the type and quantity of solvent molecules, which resulted in 44 electrons in a void volume of 274 Å$^3$, corresponding to approximately 1.7 molecules of ethanol in the unit cell. These ethanol molecules are not considered in the given chemical formula and other crystal data.

## 1. Chemical context

Among heterocyclic compounds, quinoline derivatives are of great interest because they have many interesting properties in terms of both biological and photophysical properties. For example, compounds consisting of quinine, chloroquine, amidiaquine and primaquine have antimalarial activity; 8-hydroxyquinoline is used to produce pesticides; some derivatives of quinoline are capable of emitting visible light (Sales *et al.*, 2015; dos Santos *et al.*, 2017). Currently, quinoline derivatives synthesized from multicomponent reactions including an aniline derivative, an aldehyde and a phenylalkyne with green catalysts are a trend that is receiving more attention due to a one-pot reaction with high yields. Moreover, by changing substituents in the components, it is possible to create many new derivatives of quinoline containing both aryl rings and long $\pi$-conjugation systems, and their application can be expanded (Sales *et al.*, 2015; Sharghi *et al.*, 2016). There are also many quinoline derivatives that have some interesting



photophysical properties such as metal-ion recognition (Wang *et al.*, 2020; Hojitsiriyanont *et al.*, 2021; Mohanasundaram *et al.*, 2021) or aggregation-induced emission (AIE) properties (Zhang *et al.*, 2019; Shen *et al.*, 2021; Hussain *et al.*, 2022). In addition, some quinoline derivatives have been designed that contain electron-donating atoms, N,N-donor ligands, capable of forming chelate complexes with transition-metal ions. Complexes of this type of ligands not only have more diverse structures, but also a large number of superior properties compared to the free ligands, such as higher anticancer activities (Shakir *et al.*, 2015; Wang *et al.*, 2017; Hu *et al.*, 2018) or better optical properties (Pathaw *et al.*, 2021).




**MnQP**

In this report, a new quinoline derivative, 6-(*N*,*N*-diethylamine)-4-phenyl-2(pyridin-2-yl)quinoline (**QP**), was synthesized *via* a one-pot reaction involving 4-*N*,*N*-diethylamineaniline, pyridine-2-carbaldehyde and phenylacetylene. The green catalyst used in this synthesis was montmorillonite (K-10; Fig. 1). For this compound, two electron-withdrawing groups – pyridine and phenyl – were introduced at positions C2 and C4 of the quinoline ring. In addition, an electron-donating group, *N*,*N*-diethylamino (–$NEt_2$), was also incorporated to create an electron push–pull effect. This effect contributes to an intramolecular charge transfer (ICT) during excitation *via* photon absorption. Furthermore, the organic compound contains two N-donor atoms from the quinoline and pyridine rings. As a result, the ligand can form five-membered ring chelate complexes with transition-metal ions. More specifically, $Mn^{II}$, with a $d^5$ semi-saturated electronic configuration, is able to form complexes with various coordination numbers, ranging from 4 to 7 (Jin *et al.*, 2011; Li *et al.*, 2011; Konar *et al.*, 2011; Wang *et al.*, 2017; Sääsk *et al.*, 2024). Therefore, when $Mn^{II}$ interacts with the **QP** ligand, mononuclear and polynuclear complexes with different coordination numbers can be expected. The structure of the product complex, referred to as **MnQP**, was determined using single-crystal X-ray diffraction. Furthermore, the photophysical and aggregation-induced emission (AIE) properties of both **QP** and **MnQP** were investigated using UV–vis absorption and emission spectra.

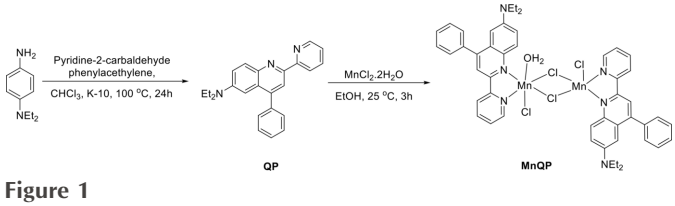



**Figure 1**
Synthesis scheme of **QP** and title compound **MnQP**.

## 2. Structural commentary

**MnQP** crystallizes in the triclinic space group $P\overline{1}$ with one complex molecule in the asymmetric unit (Fig. 2). The complex contains two $Mn^{II}$ atoms, two **QP** ligands (denoted *A* and *B*, containing atoms N1 and N4, respectively), four chlorine atoms and one water molecule. Chlorine atom Cl1 is disordered over two positions with a refined occupancy ratio of Cl1*A*:Cl1*B* = 0.680 (8):0.320 (8). For the disordered ethyl group C34–C35, the occupancy ratio refined to 0.878 (4):0.122 (4). The crystal structure contains disordered solvent molecules, which could not be modeled. The SQUEEZE procedure (Spek, 2015) was used to obtain information on the type and quantity of solvent molecules, which resulted in 44 electrons in a void volume of 274 $Å^3$, corresponding to approximately 1.7 molecules of ethanol in the unit cell.

Two bridging chlorine atoms (Cl2, Cl3) connect the two central $Mn^{II}$ atoms to form a four-membered rhomb-shaped ring. The metal···metal distance is 3.7412 (6) Å. Both $Mn^{II}$ atoms have a different coordination environment, fivefold for Mn1 and sixfold for Mn2. The coordination sphere of Mn1 is best described as distorted trigonal–bipyramidal. The equatorial positions are occupied by nitrogen atom N3 at a distance of 2.215 (2) Å, and two chlorine atoms Cl1 and Cl3 at distances of, respectively, 2.382 (2) (for Cl1*A*), 2.337 (4) (for Cl1*B*) and 2.4501 (8) Å. The axial positions are occupied by chlorine atom Cl2 at a distance of 2.4974 (7) Å and nitrogen

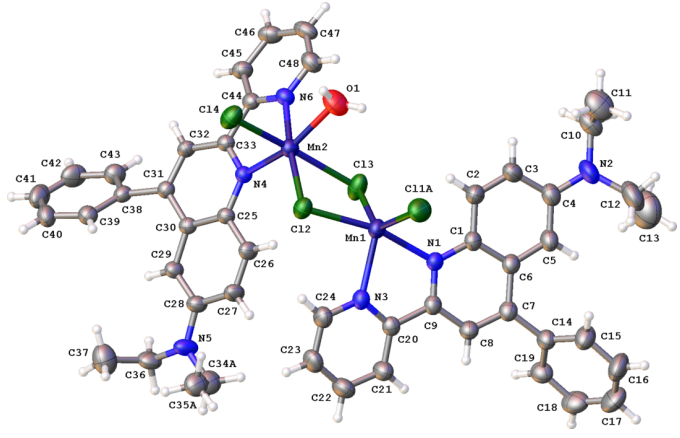



**Figure 2**
The molecular structure of **MnQP** with complete labeling of non-hydrogen atoms. Displacement ellipsoids are shown at the 30% probability level. For the Cl atom Cl1 and ethyl group C34–C35, only the part with the higher occupancy is shown.

**Table 1**
Hydrogen-bond geometry (Å, °).

*Cg1*–*Cg4* are the centroids of the C1–C6, C38–C43, N3/C20–C24 and C25–C30 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C12—H12*A*···Cl1*B*$^{i}$ | 0.97 | 2.81 | 3.734 (7) | 158 |
| C23—H23···Cl3$^{ii}$ | 0.93 | 2.74 | 3.567 (3) | 149 |
| C45—H45···Cl4$^{iii}$ | 0.93 | 2.69 | 3.563 (3) | 157 |
| C11—H11*A*···*Cg*1$^{i}$ | 0.96 | 2.97 | 3.585 (4) | 123 |
| C21—H21···*Cg*2$^{iv}$ | 0.93 | 2.89 | 3.642 (3) | 139 |
| C36—H36*B*···*Cg*3$^{iv}$ | 0.97 | 2.96 | 3.845 (3) | 153 |
| C35*B*—H35*D*···*Cg*4$^{iv}$ | 0.96 | 2.84 | 3.45 (2) | 122 |

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $x+1, y, z$; (iii) $-x, -y+2, -z+1$; (iv) $-x+1, -y+1, -z+1$.

atom N1 at a distance of 2.286 (2) Å. The Mn2 ion exhibits a distorted octahedral coordination sphere, with the equatorial plane formed by three chlorine atoms Cl2, Cl3 and Cl4 at distances of 2.6269 (8), 2.5838 (8) and 2.4354 (8) Å, respectively, and one nitrogen atom N6, at a distance of 2.257 (2) Å. One axial position is occupied by water oxygen atom O1 at a distance of 2.213 (2) Å, the other by nitrogen atom N4 at a distance of 2.3087 (19) Å.

The planar quinoline ring in ligand *A* (r.m.s. deviation = 0.014 Å) makes a dihedral angle of 9.46 (8)° with pyridine ring N3/C20–C24 and 54.84 (10)° with phenyl ring C14–C19. In ligand *B*, the quinoline ring (r.m.s. deviation = 0.061 Å) makes a significantly larger dihedral angle with the pyridine ring N6/C44–C48 [23.39 (7)°] and a smaller one with phenyl ring C38–C43 [50.15 (8)°]. The two quinoline rings are mutually inclined at an angle of 53.07 (6)°. The sum of the bond angles around N2 [358.0 (5)°] and N5 [360.0 (3)°] indicate $sp^2$ hybridization.

## 3. Supramolecular features

The crystal packing of **MnQP** is characterized by C—H···Cl and C—H···$\pi$ interactions. Inversion dimers are formed by C12—H12*A*···Cl1*B* and C45—H45···Cl4 interactions. Both dimers are part of slabs forming chains parallel to the *a* axis

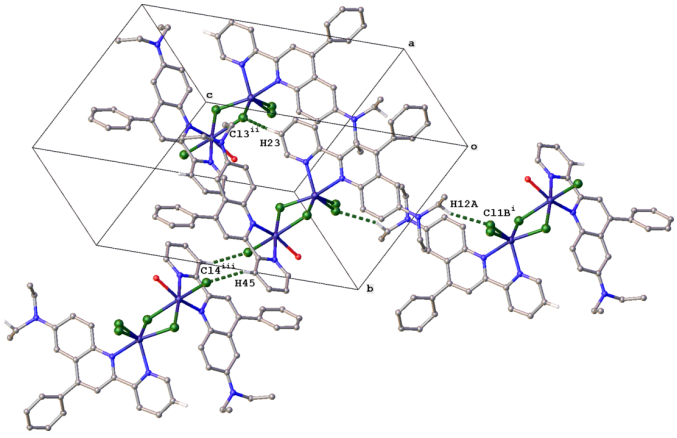



**Figure 3**
Packing diagram for **MnQP** showing C—H···Cl interactions (green lines) between molecules. For clarity, only those H atoms involved in hydrogen bonding are shown. Symmetry codes are given in Table 1.

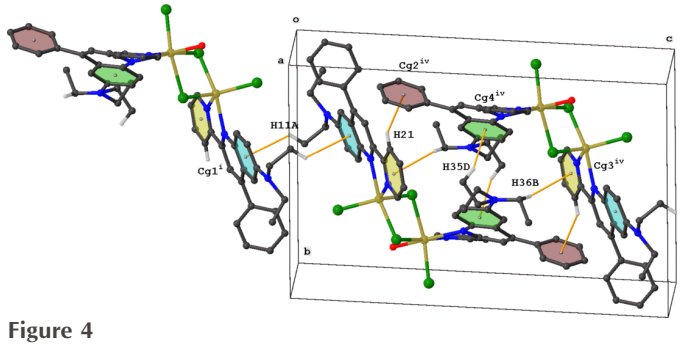



**Figure 4**
Packing diagram for **MnQP** showing the C—H···$\pi$ interactions (orange lines) between molecules. For clarity, only those H atoms involved in the interactions are shown. Symmetry codes are given in Table 1.

through C23—H23···Cl3 interactions (Fig. 3, Table 1). The packing is further stabilized by four different types of C—H···$\pi$ interactions (Fig. 4, Table 1).

The hydrogen atoms of water molecule O1 are not involved in hydrogen-bonding interactions. Significant $\pi$–$\pi$ stacking interactions between rings of neighboring molecules were not observed in this structure.

## 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.45, update of March 2024; Groom *et al.*, 2016) indicated 347 compounds incorporating a four-membered $Mn_2Cl_2$ moiety. Of these compounds, 115 also have two N atoms that bond to the each $Mn^{II}$ atom. The number of similar compounds further reduces to 69 when each $Mn^{II}$ atom bonds to an additional Cl atom. Adding an additional O atom to one of the $Mn^{II}$ atoms results in 12 complexes, all of which exhibit a coordination number of six with a distorted octahedral coordination environment for both $Mn^{II}$ atoms, and a (pseudo) inversion center at the center of the $Mn_2Cl_2$ ring. For four complexes, the O atom is part of a water molecule, where the Mn—O distance varies between 2.141 and 2.274 Å [2.323 (2) Å in **MnQP**].

## 5. Photophysical properties

The UV–vis absorption and emission spectra of **QP** and **MnQP** (10 μ*M* in THF) are shown in Fig. 5 and numerical data in Table 2. In the UV–vis spectra (Fig. 5*a*), both **QP** and **MnQP** exhibit three absorption bands with maxima at 294 nm, 351 nm, and 405 nm. These bands are attributed to the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the fused aromatic heterocycle. In the emission spectra (Fig. 5*b*), both the ligand and the complex emit light with a band at 472 nm, corresponding to blue light. Although the maximum absorption and emission wavelength do not change significantly between the ligand and the complex, the emission intensity of the complex is higher than that of the free ligand. This enhancement can be explained by the $d^5$ electronic configuration of the central $Mn^{II}$ ion, which forbids absorption of radiation in the visible range according to the Laporte rules. Additionally, the coordination of $Mn^{II}$

**Table 2**
Photophysical data for QP and MnQP (in THF, 10 μ*M*).

| Compound | Absorption | Emission | | Stokes shift |
|---|---|---|---|---|
| | $\lambda_{ABS}$(nm) / $\varepsilon$ ($10^{-3}$ $M^{-1}$.cm$^{-1}$) | $\lambda_{em}$ (nm) | Intensity (a.u.) | $\Delta\nu$ (cm$^{-1}$) |
| **QP** | 294 (21); 351 (10); 405 (11) | 472 | 55338 | 7303 |
| **MnQP** | 294 (36); 351 (18); 405 (19) | 472 | 83395 | 7340 |

with the ligand through two heterocyclic N atoms reduces rotation of the pyridine ring, leading to an increase in emission intensity from 55338 a.u. to 83395 a.u. compared to the free ligand.

The aggregation-induced emission (AIE) properties of **QP** and **MnQP** were investigated by recording photoluminescence (PL) spectra in THF/water mixtures with different water fractions (fw) at a concentration of 10 μ*M*. The results show that their fluorescent color changes from blue to green and finally turns yellow under 365 nm UV light when the water fraction increases from 0% to 99%. For the **QP** ligand, the color and intensity changes are most pronounced at a 60% water ratio (see Fig. S6 in the electronic supporting information, ESI), and the same trend is observed for the **MnQP** complex (Fig. 6). This behavior can be explained by the following factors. As the water fraction in the THF–water mixture increases, the solubility of both the ligand and the complex decreases. This reduction in solubility leads to shorter distances between molecules, which in turn promotes $\pi$–$\pi$ interactions between adjacent molecules. This interaction changes the electron density within the molecules, resulting in changes in the emission peak and intensity (Hong *et al.*, 2009).

## 6. Synthesis and crystallization

**Synthesis of 6-(*N*,*N*-diethylamine)-4-phenyl-2(pyridin-2-yl) quinoline (QP)**

To a mixture of 4-*N*,*N*-diethylamineaniline (196.8 mg, 1.2 mmol), pyridine-2-carbaldehyde (128.4 mg, 1.2 mmol), and phenylacetylene (102.0 mg, 1.0 mmol) were added montmorillonite (K-10) (500 mg) and chloroform (1 ml). The resulting reaction mixture was stirred continuously at 373 K. After 24 h, the reaction mixture was cooled down to room temperature, and extracted three times with ethylacetate/water (*v*/*v* = 1:1). The collected organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure using a rotatory evaporator to remove the solvent. The residue was then adsorbed on silicagel and purified by silica gel column chromatography with ethyl acetate/*n*-hexane (*v*/*v* = 1:10) to obtain **QP** as a dark-orange solid. The isolated yield of this cyclization reaction is 65%. The product is moderately soluble in ethanol, THF, $CHCl_3$, and DMSO. ESI–MS: 356.3 (100%) = $[QP + H]^{+\cdot}$. $^1$H NMR (600 MHz, $CDCl_3$, $\delta$ ppm): 1.16 (6H, $^3J$ = 7.2 Hz, *t*, 2 $CH_3$), 3.80 (4H, $^3J$ = 7.2 Hz, *q*, 2 $CH_2$), 6.90 (1H, $^4J$ = 3.0 Hz, d, Ar-H), 7.27 (1H, $^3J$ = 6.0 Hz, $^4J$ = 1.2 Hz, *td*, Ar-H), 7.32 (1H, $^3J$ = 9.6 Hz, $^4J$ = 3.0 Hz, *dd*, Ar-H), 7.45 (1H, $^3J$ = 7.2 Hz, *d*, Ar-H), 7.49 (2H, $^3J$ = 6.6 Hz, *t*, Ar-H), 7.60 (2H, $^3J$ = 7.2 Hz, *d*, Ar-H), 7.82 (1H, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, *td*, Ar-H), 8.07 (1H, $^3J$ = 9.6 Hz, *d*, Ar-H), 8.35 (1H, *s*, Ar-H), 8.59 (1H, $^3J$ = 7.8 Hz, *d*, Ar-H), 8.67 (1H, $^3J$ = 6.0 Hz, *d*, Ar-H). IR (KBr, cm$^{-1}$): 2965 ($\nu_{C-H\ aryl}$), 1615, 1585 ($\nu_{C=C\ aryl}$), 1504, 1435 ($\nu_{C=N\ aryl}$).

ESI–MS, FT–IR and $^1$H NMR spectra of **QP** are given in Figs. S1, S2 and S3, respectively, in the ESI.

**Synthesis of $[Mn_2(QP)_2Cl_4(H_2O)]$ (MnQP)**

$MnCl_2{\cdot}2H_2O$ (35.64 mg, 0.22 mmol) was added to a **QP** solution (70.6 mg, 0.2 mmol in 3 ml of ethanol). The resulting mixture was stirred continuously at room temperature for 3 h and became dark yellow. The solution was evaporated slowly for 48 h to obtain yellow crystals of **MnQP**. The crystals were then filtered and washed with acetone. The yield was about 52%. The crystals are moderately soluble in ethanol, THF, $CHCl_3$ and DMSO. ESI–MS: 729.3 (65%) = $[Mn_2(QP)_2Cl_4(H_2O)$-QP+2DMSO-$H_2O$-$H]^+$; 937.8 (20%) = $[Mn_2(QP)_2Cl_4(H_2O)$-$Cl]^+$. IR (KBr, cm$^{-1}$): 3407 ($\nu_{O-H}$ $H_2O$), 2971 ($\nu_{C-H\ aryl}$), 1614, 1599 ($\nu_{C=C\ aryl}$), 1506, 1483 ($\nu_{C=N\ aryl}$).

ESI–MS and FT–IR spectra of **MnQP** are given in Figs. S4 and S5, respectively, in the ESI.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms were included as

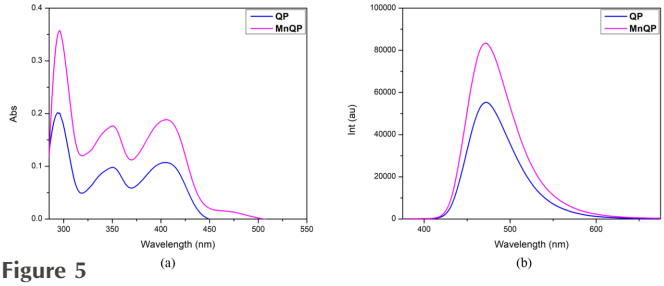



**Figure 5**
(*a*) UV–vis absorption and (*b*) emission spectra of **QP** and **MnQP** (10 μ*M* in THF, $\lambda_{ex}$ = 360 nm).

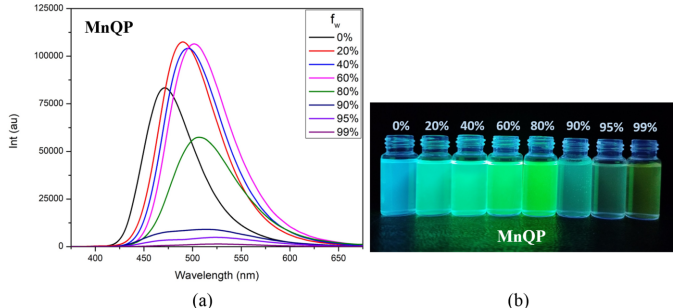



**Figure 6**
(*a*) Emission spectra and (*b*) fluorescent color change of **MnQP** with a concentration of 10 μ*M* in different fractions of water in a THF–water mixture.

**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Mn_2Cl_4(C_{24}H_{23}N_3)_2(H_2O)]$ |
| $M_r$ | 976.60 |
| Crystal system, space group | Triclinic, $P\overline{1}$ |
| Temperature (K) | 294 |
| $a, b, c$ (Å) | 8.7491 (2), 13.2133 (3), 21.3793 (5) |
| $\alpha, \beta, \gamma$ (°) | 88.914 (2), 82.290 (2), 88.989 (2) |
| $V$ (Å$^3$) | 2448.48 (10) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.78 |
| Crystal size (mm) | 0.4 × 0.15 × 0.05 |
| Data collection | |
| Diffractometer | SuperNova, Single source at offset/far, Eos |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2024) |
| $T_{min}$, $T_{max}$ | 0.606, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 50282, 9973, 7946 |
| $R_{int}$ | 0.034 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.625 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.044, 0.139, 0.86 |
| No. of reflections | 9973 |
| No. of parameters | 560 |
| No. of restraints | 18 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.86, −0.47 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

riding contributions in idealized positions with isotropic displacement parameters $U_{iso}$(H) = 1.2 $U_{eq}$(C) (1.5 for methyl groups). The Cl1 atom and ethyl group C34–C35 were found to be disordered over two positions with refined occupancies of 0.680 (8) and 0.320 (8) for Cl1, and 0.878 (4) and 0.122 (4) for ethyl group C34–C35. The H atoms of the water molecule were located in a difference electron-density map and refined with $U_{iso}$(H) = 1.5$U_{eq}$(O) and O—H distances restrained to 0.82 Å. RIGU and DELU restraints were used for atoms N2, Cl2 and Cl3 to impose reasonable relative motion of these atoms. Additional electron density was localized in voids (274 Å$^3$ total potential accessible volume) summing up to 44 electrons, which corresponds to approximately 1.7 molecules of ethanol per unit cell. The electron density associated with the disordered ethanol molecules was removed with the SQUEEZE (Spek, 2015) routine in *PLATON* (Spek, 2020). These ethanol molecules are not considered in the given chemical formula and other crystal data.

## Acknowledgements

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# supporting information

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# Synthesis, crystal structure and photophysical properties of a dinuclear $Mn^{II}$ complex with 6-(diethylamino)-4-phenyl-2-(pyridin-2-yl)quinoline

**Hai Le Thi Hong, Duong Hoang Tuan, Anh Nguyen Duc, Hien Nguyen and Luc Van Meervelt**

## Computing details

**Aqua-1$\kappa O$-di-$\mu$-chlorido-1:2$\kappa^4 Cl$:$Cl$-dichlorido-1$\kappa Cl$,2$\kappa Cl$-bis[6-(diethylamino)-4-phenyl-2-(pyridin-2-yl)quinoline]-1$\kappa^2 N^1$,$N^2$;2$\kappa^2 N^1$,$N^2$-dimanganese(II)**

*Crystal data*

$[Mn_2Cl_4(C_{24}H_{23}N_3)_2(H_2O)]$
$M_r$ = 976.60
Triclinic, $P\overline{1}$
$a$ = 8.7491 (2) Å
$b$ = 13.2133 (3) Å
$c$ = 21.3793 (5) Å
$\alpha$ = 88.914 (2)°
$\beta$ = 82.290 (2)°
$\gamma$ = 88.989 (2)°
$V$ = 2448.48 (10) Å$^3$
$Z$ = 2
$F(000)$ = 1008
$D_x$ = 1.325 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 20239 reflections
$\theta$ = 3.6–27.7°
$\mu$ = 0.78 mm$^{-1}$
$T$ = 294 K
Plate, yellow
0.4 × 0.15 × 0.05 mm

*Data collection*

SuperNova, Single source at offset/far, Eos diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 15.9566 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2024)
$T_{min}$ = 0.606, $T_{max}$ = 1.000
50282 measured reflections
9973 independent reflections
7946 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.034
$\theta_{max}$ = 26.4°, $\theta_{min}$ = 3.3°
$h$ = −10→10
$k$ = −16→16
$l$ = −26→26

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.139
$S$ = 0.86
9973 reflections
560 parameters
18 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0889P)^2 + 2.333P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.86 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.47 e Å$^{-3}$

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Mn1 | 0.35314 (5) | 0.65406 (3) | 0.22302 (2) | 0.03955 (12) | |
| Cl1A | 0.3891 (5) | 0.7046 (2) | 0.11458 (10) | 0.0598 (4) | 0.680 (8) |
| Cl1B | 0.3379 (8) | 0.7186 (4) | 0.1215 (2) | 0.0598 (4) | 0.320 (8) |
| O1 | 0.0739 (3) | 0.8996 (2) | 0.25271 (12) | 0.0689 (7) | |
| H1A | 0.101 (5) | 0.9574 (15) | 0.243 (2) | 0.103* | |
| H1B | 0.072 (6) | 0.866 (3) | 0.2203 (14) | 0.103* | |
| N1 | 0.3023 (2) | 0.49080 (16) | 0.20012 (10) | 0.0365 (5) | |
| C1 | 0.1824 (3) | 0.4612 (2) | 0.17034 (12) | 0.0383 (5) | |
| Mn2 | 0.17320 (4) | 0.84639 (3) | 0.33759 (2) | 0.03688 (12) | |
| Cl2 | 0.44135 (8) | 0.81104 (5) | 0.26973 (3) | 0.04346 (16) | |
| N2 | −0.1917 (3) | 0.3857 (2) | 0.07467 (15) | 0.0666 (8) | |
| C2 | 0.0623 (3) | 0.5316 (2) | 0.16218 (14) | 0.0482 (7) | |
| H2 | 0.066162 | 0.596571 | 0.177875 | 0.058* | |
| Cl3 | 0.12894 (9) | 0.66307 (6) | 0.30488 (4) | 0.0539 (2) | |
| N3 | 0.5448 (2) | 0.55925 (16) | 0.25097 (10) | 0.0388 (5) | |
| C3 | −0.0584 (3) | 0.5064 (2) | 0.13192 (14) | 0.0506 (7) | |
| H3 | −0.135308 | 0.554530 | 0.127541 | 0.061* | |
| Cl4 | 0.25143 (9) | 1.01982 (6) | 0.35077 (4) | 0.05338 (19) | |
| N4 | 0.1805 (2) | 0.79905 (15) | 0.44166 (9) | 0.0314 (4) | |
| C4 | −0.0703 (3) | 0.4089 (2) | 0.10692 (13) | 0.0475 (7) | |
| N5 | 0.6580 (3) | 0.5855 (2) | 0.53537 (11) | 0.0541 (6) | |
| C5 | 0.0438 (3) | 0.3380 (2) | 0.11605 (13) | 0.0461 (6) | |
| H5 | 0.035832 | 0.272545 | 0.101729 | 0.055* | |
| N6 | −0.0657 (2) | 0.86758 (16) | 0.39068 (10) | 0.0374 (5) | |
| C6 | 0.1720 (3) | 0.36243 (19) | 0.14655 (12) | 0.0379 (5) | |
| C7 | 0.2938 (3) | 0.29213 (19) | 0.15545 (12) | 0.0391 (6) | |
| C8 | 0.4082 (3) | 0.32372 (19) | 0.18789 (12) | 0.0392 (6) | |
| H8 | 0.485393 | 0.278036 | 0.196120 | 0.047* | |
| C9 | 0.4120 (3) | 0.42339 (19) | 0.20908 (11) | 0.0360 (5) | |
| C10 | −0.3167 (4) | 0.4582 (3) | 0.06752 (15) | 0.0582 (8) | |
| H10A | −0.338472 | 0.496987 | 0.105847 | 0.070* | |
| H10B | −0.408843 | 0.421213 | 0.062418 | 0.070* | |
| C11 | −0.2811 (5) | 0.5301 (3) | 0.01241 (18) | 0.0830 (12) | |
| H11A | −0.260119 | 0.492405 | −0.025818 | 0.125* | |
| H11B | −0.192547 | 0.569133 | 0.017930 | 0.125* | |
| H11C | −0.368005 | 0.574673 | 0.009902 | 0.125* | |
| C12 | −0.1760 (5) | 0.2956 (3) | 0.0310 (2) | 0.0854 (12) | |
| H12A | −0.225658 | 0.311567 | −0.006007 | 0.103* | |
| H12B | −0.067625 | 0.281812 | 0.017003 | 0.103* | |

| | | | | | |
|---|---|---|---|---|---|
| C13 | −0.2449 (7) | 0.2072 (4) | 0.0624 (3) | 0.128 (2) | |
| H13A | −0.199280 | 0.193234 | 0.100073 | 0.192* | |
| H13B | −0.227740 | 0.150391 | 0.034807 | 0.192* | |
| H13C | −0.353785 | 0.218854 | 0.073176 | 0.192* | |
| C14 | 0.3028 (3) | 0.1878 (2) | 0.12996 (13) | 0.0426 (6) | |
| C15 | 0.3031 (4) | 0.1708 (2) | 0.06598 (16) | 0.0604 (8) | |
| H15 | 0.287552 | 0.224799 | 0.038894 | 0.073* | |
| C16 | 0.3263 (5) | 0.0746 (3) | 0.04233 (19) | 0.0793 (12) | |
| H16 | 0.325846 | 0.064160 | −0.000539 | 0.095* | |
| C17 | 0.3502 (5) | −0.0066 (3) | 0.0820 (2) | 0.0773 (11) | |
| H17 | 0.365477 | −0.071499 | 0.065966 | 0.093* | |
| C18 | 0.3512 (4) | 0.0093 (2) | 0.14495 (19) | 0.0652 (9) | |
| H18 | 0.368046 | −0.044899 | 0.171690 | 0.078* | |
| C19 | 0.3273 (3) | 0.1054 (2) | 0.16911 (15) | 0.0509 (7) | |
| H19 | 0.327561 | 0.115159 | 0.212065 | 0.061* | |
| C20 | 0.5421 (3) | 0.45903 (19) | 0.24069 (11) | 0.0351 (5) | |
| C21 | 0.6551 (3) | 0.3940 (2) | 0.25902 (14) | 0.0480 (7) | |
| H21 | 0.651441 | 0.324875 | 0.252079 | 0.058* | |
| C22 | 0.7730 (3) | 0.4332 (3) | 0.28766 (16) | 0.0555 (8) | |
| H22 | 0.849573 | 0.390617 | 0.300053 | 0.067* | |
| C23 | 0.7765 (3) | 0.5349 (2) | 0.29771 (15) | 0.0519 (7) | |
| H23 | 0.855142 | 0.562503 | 0.316873 | 0.062* | |
| C24 | 0.6613 (3) | 0.5953 (2) | 0.27886 (14) | 0.0470 (6) | |
| H24 | 0.663814 | 0.664509 | 0.285689 | 0.056* | |
| C25 | 0.3019 (3) | 0.75430 (18) | 0.46657 (11) | 0.0312 (5) | |
| C26 | 0.4121 (3) | 0.6987 (2) | 0.42594 (12) | 0.0388 (6) | |
| H26 | 0.404769 | 0.697817 | 0.382954 | 0.047* | |
| C27 | 0.5282 (3) | 0.6468 (2) | 0.44870 (12) | 0.0435 (6) | |
| H27 | 0.599206 | 0.611244 | 0.420730 | 0.052* | |
| C28 | 0.5450 (3) | 0.6448 (2) | 0.51415 (12) | 0.0402 (6) | |
| C29 | 0.4400 (3) | 0.70200 (19) | 0.55394 (11) | 0.0361 (5) | |
| H29 | 0.450440 | 0.703967 | 0.596623 | 0.043* | |
| C30 | 0.3186 (3) | 0.75706 (17) | 0.53179 (11) | 0.0314 (5) | |
| C31 | 0.2053 (3) | 0.81444 (18) | 0.57144 (11) | 0.0313 (5) | |
| C32 | 0.0798 (3) | 0.85298 (18) | 0.54550 (11) | 0.0336 (5) | |
| H32 | 0.001934 | 0.887326 | 0.570944 | 0.040* | |
| C33 | 0.0682 (3) | 0.84097 (17) | 0.48098 (11) | 0.0318 (5) | |
| C34A | 0.7695 (5) | 0.5291 (3) | 0.49221 (17) | 0.0598 (4) | 0.878 (4) |
| H34A | 0.716880 | 0.495813 | 0.461332 | 0.072* | 0.878 (4) |
| H34B | 0.819456 | 0.477394 | 0.515525 | 0.072* | 0.878 (4) |
| C35A | 0.8880 (5) | 0.5987 (3) | 0.45924 (17) | 0.0598 (4) | 0.878 (4) |
| H35A | 0.837950 | 0.651735 | 0.437884 | 0.090* | 0.878 (4) |
| H35B | 0.957178 | 0.561486 | 0.429056 | 0.090* | 0.878 (4) |
| H35C | 0.945156 | 0.627778 | 0.489612 | 0.090* | 0.878 (4) |
| C34B | 0.8079 (18) | 0.5859 (16) | 0.4945 (10) | 0.0598 (4) | 0.122 (4) |
| H34C | 0.890775 | 0.589382 | 0.520309 | 0.072* | 0.122 (4) |
| H34D | 0.813426 | 0.644931 | 0.466687 | 0.072* | 0.122 (4) |
| C35B | 0.826 (3) | 0.4903 (17) | 0.4557 (9) | 0.0598 (4) | 0.122 (4) |

| | | | | | |
|---|---|---|---|---|---|
| H35D | 0.828382 | 0.432266 | 0.483290 | 0.090* | 0.122 (4) |
| H35E | 0.920930 | 0.492781 | 0.427229 | 0.090* | 0.122 (4) |
| H35F | 0.741117 | 0.485305 | 0.431911 | 0.090* | 0.122 (4) |
| C36 | 0.6734 (4) | 0.5767 (2) | 0.60222 (14) | 0.0530 (7) | |
| H36A | 0.722257 | 0.511940 | 0.609811 | 0.064* | |
| H36B | 0.571034 | 0.576515 | 0.626112 | 0.064* | |
| C37 | 0.7654 (5) | 0.6594 (3) | 0.62720 (18) | 0.0799 (11) | |
| H37A | 0.863950 | 0.664467 | 0.601628 | 0.120* | |
| H37B | 0.779985 | 0.643394 | 0.670001 | 0.120* | |
| H37C | 0.710372 | 0.722741 | 0.625797 | 0.120* | |
| C38 | 0.2191 (3) | 0.83535 (18) | 0.63866 (11) | 0.0345 (5) | |
| C39 | 0.3567 (3) | 0.8713 (2) | 0.65593 (12) | 0.0405 (6) | |
| H39 | 0.443295 | 0.876552 | 0.625739 | 0.049* | |
| C40 | 0.3653 (4) | 0.8991 (2) | 0.71739 (14) | 0.0514 (7) | |
| H40 | 0.456951 | 0.924070 | 0.728097 | 0.062* | |
| C41 | 0.2390 (4) | 0.8900 (3) | 0.76260 (14) | 0.0613 (9) | |
| H41 | 0.245125 | 0.908451 | 0.803944 | 0.074* | |
| C42 | 0.1030 (4) | 0.8535 (3) | 0.74660 (14) | 0.0589 (8) | |
| H42 | 0.017851 | 0.846313 | 0.777370 | 0.071* | |
| C43 | 0.0927 (3) | 0.8274 (2) | 0.68500 (13) | 0.0456 (6) | |
| H43 | −0.000234 | 0.804239 | 0.674505 | 0.055* | |
| C44 | −0.0744 (3) | 0.87005 (18) | 0.45391 (12) | 0.0338 (5) | |
| C45 | −0.2125 (3) | 0.8899 (2) | 0.49184 (13) | 0.0416 (6) | |
| H45 | −0.215800 | 0.893448 | 0.535407 | 0.050* | |
| C46 | −0.3456 (3) | 0.9044 (2) | 0.46411 (15) | 0.0480 (7) | |
| H46 | −0.439540 | 0.916770 | 0.488922 | 0.058* | |
| C47 | −0.3376 (3) | 0.9002 (2) | 0.39932 (15) | 0.0495 (7) | |
| H47 | −0.425572 | 0.909121 | 0.379625 | 0.059* | |
| C48 | −0.1953 (3) | 0.8826 (2) | 0.36457 (14) | 0.0486 (7) | |
| H48 | −0.189055 | 0.880983 | 0.320833 | 0.058* | |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Mn1 | 0.0468 (2) | 0.0371 (2) | 0.0362 (2) | 0.00307 (17) | −0.01036 (17) | −0.00673 (16) |
| Cl1A | 0.0741 (13) | 0.0631 (8) | 0.0429 (6) | 0.0085 (8) | −0.0122 (7) | 0.0016 (5) |
| Cl1B | 0.0741 (13) | 0.0631 (8) | 0.0429 (6) | 0.0085 (8) | −0.0122 (7) | 0.0016 (5) |
| O1 | 0.0712 (16) | 0.0835 (19) | 0.0555 (14) | 0.0005 (14) | −0.0230 (12) | 0.0105 (13) |
| N1 | 0.0404 (11) | 0.0364 (11) | 0.0340 (10) | 0.0031 (9) | −0.0089 (9) | −0.0066 (8) |
| C1 | 0.0423 (14) | 0.0410 (14) | 0.0331 (12) | 0.0003 (11) | −0.0100 (10) | −0.0046 (10) |
| Mn2 | 0.0388 (2) | 0.0400 (2) | 0.0325 (2) | 0.00306 (16) | −0.00725 (15) | −0.00383 (15) |
| Cl2 | 0.0467 (4) | 0.0396 (3) | 0.0439 (3) | −0.0031 (3) | −0.0039 (3) | −0.0069 (3) |
| N2 | 0.0637 (17) | 0.0703 (19) | 0.0751 (19) | 0.0021 (14) | −0.0430 (15) | −0.0104 (14) |
| C2 | 0.0512 (16) | 0.0470 (16) | 0.0492 (16) | 0.0089 (13) | −0.0165 (13) | −0.0126 (13) |
| Cl3 | 0.0507 (4) | 0.0526 (4) | 0.0563 (4) | −0.0139 (3) | 0.0052 (3) | −0.0198 (3) |
| N3 | 0.0409 (12) | 0.0381 (12) | 0.0386 (11) | −0.0021 (9) | −0.0085 (9) | −0.0060 (9) |
| C3 | 0.0471 (16) | 0.0583 (18) | 0.0496 (16) | 0.0115 (13) | −0.0185 (13) | −0.0098 (13) |
| Cl4 | 0.0548 (4) | 0.0441 (4) | 0.0592 (4) | −0.0025 (3) | 0.0015 (3) | −0.0111 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N4 | 0.0322 (10) | 0.0324 (10) | 0.0304 (10) | 0.0026 (8) | −0.0067 (8) | −0.0021 (8) |
| C4 | 0.0497 (16) | 0.0528 (17) | 0.0427 (15) | −0.0033 (13) | −0.0154 (12) | −0.0023 (12) |
| N5 | 0.0552 (15) | 0.0649 (16) | 0.0421 (13) | 0.0296 (12) | −0.0104 (11) | −0.0019 (11) |
| C5 | 0.0550 (17) | 0.0411 (15) | 0.0457 (15) | −0.0044 (12) | −0.0185 (13) | −0.0030 (12) |
| N6 | 0.0354 (11) | 0.0375 (11) | 0.0412 (12) | 0.0032 (9) | −0.0121 (9) | −0.0008 (9) |
| C6 | 0.0451 (14) | 0.0363 (13) | 0.0331 (12) | −0.0010 (11) | −0.0083 (10) | −0.0004 (10) |
| C7 | 0.0478 (15) | 0.0351 (13) | 0.0354 (13) | −0.0021 (11) | −0.0089 (11) | 0.0007 (10) |
| C8 | 0.0441 (14) | 0.0345 (13) | 0.0405 (13) | 0.0018 (11) | −0.0110 (11) | 0.0000 (10) |
| C9 | 0.0411 (13) | 0.0367 (13) | 0.0308 (12) | −0.0019 (10) | −0.0068 (10) | −0.0013 (10) |
| C10 | 0.0467 (17) | 0.077 (2) | 0.0538 (18) | −0.0056 (15) | −0.0180 (14) | 0.0053 (16) |
| C11 | 0.088 (3) | 0.102 (3) | 0.060 (2) | −0.006 (2) | −0.014 (2) | 0.018 (2) |
| C12 | 0.088 (3) | 0.093 (3) | 0.087 (3) | −0.010 (2) | −0.054 (2) | −0.003 (2) |
| C13 | 0.131 (5) | 0.113 (4) | 0.147 (5) | −0.035 (4) | −0.039 (4) | 0.000 (4) |
| C14 | 0.0468 (15) | 0.0362 (14) | 0.0470 (15) | −0.0014 (11) | −0.0146 (12) | −0.0023 (11) |
| C15 | 0.089 (2) | 0.0436 (17) | 0.0519 (17) | 0.0053 (16) | −0.0220 (16) | −0.0061 (13) |
| C16 | 0.121 (3) | 0.057 (2) | 0.065 (2) | 0.010 (2) | −0.030 (2) | −0.0248 (18) |
| C17 | 0.099 (3) | 0.0407 (18) | 0.095 (3) | 0.0075 (18) | −0.019 (2) | −0.0166 (18) |
| C18 | 0.071 (2) | 0.0390 (17) | 0.087 (3) | 0.0017 (15) | −0.0154 (19) | 0.0088 (16) |
| C19 | 0.0550 (17) | 0.0434 (16) | 0.0563 (17) | −0.0001 (13) | −0.0156 (14) | 0.0044 (13) |
| C20 | 0.0344 (12) | 0.0385 (13) | 0.0320 (12) | −0.0027 (10) | −0.0028 (9) | −0.0015 (10) |
| C21 | 0.0484 (16) | 0.0419 (15) | 0.0567 (17) | 0.0026 (12) | −0.0178 (13) | −0.0021 (13) |
| C22 | 0.0441 (16) | 0.0583 (19) | 0.068 (2) | 0.0048 (14) | −0.0215 (14) | −0.0008 (15) |
| C23 | 0.0396 (15) | 0.0601 (19) | 0.0588 (18) | −0.0070 (13) | −0.0156 (13) | −0.0073 (14) |
| C24 | 0.0423 (15) | 0.0476 (16) | 0.0530 (16) | −0.0033 (12) | −0.0116 (12) | −0.0087 (13) |
| C25 | 0.0295 (11) | 0.0319 (12) | 0.0323 (12) | 0.0025 (9) | −0.0050 (9) | −0.0002 (9) |
| C26 | 0.0406 (14) | 0.0460 (15) | 0.0296 (12) | 0.0077 (11) | −0.0052 (10) | −0.0033 (10) |
| C27 | 0.0388 (14) | 0.0531 (16) | 0.0383 (14) | 0.0148 (12) | −0.0051 (11) | −0.0078 (12) |
| C28 | 0.0374 (13) | 0.0424 (15) | 0.0410 (14) | 0.0091 (11) | −0.0078 (11) | −0.0003 (11) |
| C29 | 0.0380 (13) | 0.0403 (14) | 0.0303 (12) | 0.0075 (10) | −0.0069 (10) | −0.0001 (10) |
| C30 | 0.0311 (11) | 0.0303 (12) | 0.0329 (12) | 0.0011 (9) | −0.0045 (9) | 0.0002 (9) |
| C31 | 0.0313 (12) | 0.0308 (12) | 0.0317 (11) | −0.0003 (9) | −0.0039 (9) | −0.0013 (9) |
| C32 | 0.0315 (12) | 0.0345 (13) | 0.0344 (12) | 0.0051 (10) | −0.0031 (9) | −0.0053 (10) |
| C33 | 0.0314 (12) | 0.0298 (12) | 0.0346 (12) | 0.0024 (9) | −0.0061 (9) | −0.0012 (9) |
| C34A | 0.0741 (13) | 0.0631 (8) | 0.0429 (6) | 0.0085 (8) | −0.0122 (7) | 0.0016 (5) |
| C35A | 0.0741 (13) | 0.0631 (8) | 0.0429 (6) | 0.0085 (8) | −0.0122 (7) | 0.0016 (5) |
| C34B | 0.0741 (13) | 0.0631 (8) | 0.0429 (6) | 0.0085 (8) | −0.0122 (7) | 0.0016 (5) |
| C35B | 0.0741 (13) | 0.0631 (8) | 0.0429 (6) | 0.0085 (8) | −0.0122 (7) | 0.0016 (5) |
| C36 | 0.0552 (17) | 0.0551 (18) | 0.0505 (17) | 0.0177 (14) | −0.0166 (13) | 0.0058 (13) |
| C37 | 0.083 (3) | 0.098 (3) | 0.061 (2) | −0.013 (2) | −0.0170 (19) | −0.004 (2) |
| C38 | 0.0393 (13) | 0.0320 (12) | 0.0321 (12) | 0.0066 (10) | −0.0055 (10) | −0.0023 (9) |
| C39 | 0.0430 (14) | 0.0402 (14) | 0.0391 (13) | 0.0027 (11) | −0.0088 (11) | −0.0007 (11) |
| C40 | 0.0636 (19) | 0.0488 (17) | 0.0466 (16) | 0.0016 (14) | −0.0248 (14) | −0.0054 (13) |
| C41 | 0.093 (3) | 0.0584 (19) | 0.0349 (15) | 0.0158 (18) | −0.0183 (16) | −0.0083 (13) |
| C42 | 0.064 (2) | 0.070 (2) | 0.0378 (15) | 0.0162 (16) | 0.0062 (14) | −0.0025 (14) |
| C43 | 0.0440 (15) | 0.0521 (17) | 0.0399 (14) | 0.0035 (12) | −0.0023 (11) | −0.0013 (12) |
| C44 | 0.0326 (12) | 0.0291 (12) | 0.0407 (13) | 0.0011 (9) | −0.0089 (10) | −0.0025 (10) |
| C45 | 0.0365 (13) | 0.0435 (15) | 0.0446 (14) | 0.0064 (11) | −0.0055 (11) | −0.0028 (11) |
| C46 | 0.0317 (13) | 0.0477 (16) | 0.0632 (18) | 0.0058 (11) | −0.0037 (12) | 0.0046 (13) |

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|---|---|---|---|---|---|---|
| C47 | 0.0352 (14) | 0.0475 (16) | 0.069 (2) | 0.0007 (12) | −0.0213 (13) | 0.0081 (14) |
| C48 | 0.0457 (16) | 0.0544 (17) | 0.0487 (16) | 0.0004 (13) | −0.0179 (13) | 0.0010 (13) |

*Geometric parameters (Å, º)*

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|---|---|---|---|
| Mn1—Cl1A | 2.382 (2) | C12—C13 | 1.437 (7) |
| Mn1—Cl1B | 2.337 (4) | C13—H13A | 0.9600 |
| Mn1—N1 | 2.286 (2) | C13—H13B | 0.9600 |
| Mn1—Cl2 | 2.4974 (7) | C13—H13C | 0.9600 |
| Mn1—Cl3 | 2.4501 (8) | C14—C15 | 1.390 (4) |
| Mn1—N3 | 2.215 (2) | C14—C19 | 1.392 (4) |
| C34Aa—H34A | 0.9700 | C15—H15 | 0.9300 |
| C34Aa—H34B | 0.9700 | C15—C16 | 1.378 (5) |
| C34Aa—C35A | 1.494 (6) | C16—H16 | 0.9300 |
| C35Aa—H35A | 0.9600 | C16—C17 | 1.387 (5) |
| C35Aa—H35B | 0.9600 | C17—H17 | 0.9300 |
| C35Aa—H35C | 0.9600 | C17—C18 | 1.367 (5) |
| C34Bb—H34C | 0.9700 | C18—H18 | 0.9300 |
| C34Bb—H34D | 0.9700 | C18—C19 | 1.382 (5) |
| C34Bb—C35B | 1.520 (10) | C19—H19 | 0.9300 |
| C35Bb—H35D | 0.9600 | C20—C21 | 1.390 (4) |
| C35Bb—H35E | 0.9600 | C21—H21 | 0.9300 |
| C35Bb—H35F | 0.9600 | C21—C22 | 1.381 (4) |
| O1—H1A | 0.816 (10) | C22—H22 | 0.9300 |
| O1—H1B | 0.832 (10) | C22—C23 | 1.366 (4) |
| O1—Mn2 | 2.213 (2) | C23—H23 | 0.9300 |
| N1—C1 | 1.364 (3) | C23—C24 | 1.373 (4) |
| N1—C9 | 1.328 (3) | C24—H24 | 0.9300 |
| C1—C2 | 1.418 (4) | C25—C26 | 1.413 (3) |
| C1—C6 | 1.418 (4) | C25—C30 | 1.423 (3) |
| Mn2—Cl2 | 2.6269 (8) | C26—H26 | 0.9300 |
| Mn2—Cl3 | 2.5838 (8) | C26—C27 | 1.354 (4) |
| Mn2—Cl4 | 2.4354 (8) | C27—H27 | 0.9300 |
| Mn2—N4 | 2.3087 (19) | C27—C28 | 1.426 (4) |
| Mn2—N6 | 2.257 (2) | C28—C29 | 1.389 (4) |
| N2—C4 | 1.383 (4) | C29—H29 | 0.9300 |
| N2—C10 | 1.462 (4) | C29—C30 | 1.406 (3) |
| N2—C12 | 1.521 (5) | C30—C31 | 1.432 (3) |
| C2—H2 | 0.9300 | C31—C32 | 1.380 (3) |
| C2—C3 | 1.360 (4) | C31—C38 | 1.490 (3) |
| N3—C20 | 1.348 (3) | C32—H32 | 0.9300 |
| N3—C24 | 1.346 (3) | C32—C33 | 1.409 (3) |
| C3—H3 | 0.9300 | C33—C44 | 1.485 (3) |
| C3—C4 | 1.415 (4) | C36—H36A | 0.9700 |
| N4—C25 | 1.371 (3) | C36—H36B | 0.9700 |
| N4—C33 | 1.325 (3) | C36—C37 | 1.515 (5) |
| C4—C5 | 1.387 (4) | C37—H37A | 0.9600 |
| N5—C28 | 1.370 (3) | C37—H37B | 0.9600 |

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| N5—C34A | 1.455 (4) | C37—H37C | 0.9600 |
| N5—C34B | 1.474 (10) | C38—C39 | 1.398 (4) |
| N5—C36 | 1.456 (4) | C38—C43 | 1.387 (4) |
| C5—H5 | 0.9300 | C39—H39 | 0.9300 |
| C5—C6 | 1.415 (4) | C39—C40 | 1.383 (4) |
| N6—C44 | 1.345 (3) | C40—H40 | 0.9300 |
| N6—C48 | 1.339 (3) | C40—C41 | 1.373 (5) |
| C6—C7 | 1.431 (4) | C41—H41 | 0.9300 |
| C7—C8 | 1.367 (4) | C41—C42 | 1.379 (5) |
| C7—C14 | 1.489 (4) | C42—H42 | 0.9300 |
| C8—H8 | 0.9300 | C42—C43 | 1.383 (4) |
| C8—C9 | 1.403 (4) | C43—H43 | 0.9300 |
| C9—C20 | 1.487 (3) | C44—C45 | 1.386 (3) |
| C10—H10A | 0.9700 | C45—H45 | 0.9300 |
| C10—H10B | 0.9700 | C45—C46 | 1.385 (4) |
| C10—C11 | 1.502 (5) | C46—H46 | 0.9300 |
| C11—H11A | 0.9600 | C46—C47 | 1.380 (4) |
| C11—H11B | 0.9600 | C47—H47 | 0.9300 |
| C11—H11C | 0.9600 | C47—C48 | 1.380 (4) |
| C12—H12A | 0.9700 | C48—H48 | 0.9300 |
| C12—H12B | 0.9700 | | |

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| CL1Aa—Mn1—Cl2 | 99.12 (6) | N2—C12—H12A | 109.4 |
| N1—Mn1—Cl1A | 92.70 (8) | N2—C12—H12B | 109.4 |
| CL1Bb—Mn1—Cl2 | 97.93 (15) | H12A—C12—H12B | 108.0 |
| CL1Aa—Mn1—Cl3 | 132.16 (10) | C13—C12—N2 | 111.0 (4) |
| N1—Mn1—Cl1B | 95.38 (16) | C13—C12—H12A | 109.4 |
| N1—Mn1—Cl2 | 165.37 (6) | C13—C12—H12B | 109.4 |
| N1—Mn1—Cl3 | 92.21 (6) | C12—C13—H13A | 109.5 |
| Cl3—Mn1—Cl2 | 86.25 (2) | C12—C13—H13B | 109.5 |
| N3—Mn1—Cl1A | 113.64 (12) | C12—C13—H13C | 109.5 |
| N3—Mn1—Cl1B | 125.41 (18) | H13A—C13—H13B | 109.5 |
| N3—Mn1—N1 | 73.33 (8) | H13A—C13—H13C | 109.5 |
| N3—Mn1—Cl2 | 93.91 (6) | H13B—C13—H13C | 109.5 |
| N3—Mn1—Cl3 | 113.33 (6) | C15—C14—C7 | 121.4 (2) |
| CL1Bb—Mn1—Cl3 | 120.46 (18) | C15—C14—C19 | 118.2 (3) |
| H1A—O1—H1B | 111 (5) | C19—C14—C7 | 120.0 (2) |
| C35Aa—C34Aa—H34A | 109.6 | C14—C15—H15 | 119.7 |
| H34Aa—C34Aa—H34B | 108.1 | C16—C15—C14 | 120.6 (3) |
| Mn2—O1—H1A | 110 (4) | C16—C15—H15 | 119.7 |
| C35Aa—C34Aa—H34B | 109.6 | C15—C16—H16 | 119.8 |
| C34Aa—C35Aa—H35A | 109.5 | C15—C16—C17 | 120.4 (4) |
| H35Aa—C35Aa—H35B | 109.5 | C17—C16—H16 | 119.8 |
| C34Aa—C35Aa—H35B | 109.5 | C16—C17—H17 | 120.3 |
| H35Ba—C35Aa—H35C | 109.5 | C18—C17—C16 | 119.5 (3) |
| H35Aa—C35Aa—H35C | 109.5 | C18—C17—H17 | 120.3 |
| Mn2—O1—H1B | 125 (3) | C17—C18—H18 | 119.8 |
| C1—N1—Mn1 | 125.31 (17) | C17—C18—C19 | 120.5 (3) |

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| C9—N1—Mn1 | 115.29 (16) | C19—C18—H18 | 119.8 |
| C9—N1—C1 | 118.7 (2) | C14—C19—H19 | 119.6 |
| N1—C1—C2 | 119.2 (2) | C18—C19—C14 | 120.8 (3) |
| N1—C1—C6 | 123.0 (2) | C18—C19—H19 | 119.6 |
| C6—C1—C2 | 117.8 (2) | N3—C20—C9 | 116.1 (2) |
| O1—Mn2—Cl2 | 91.02 (8) | N3—C20—C21 | 121.2 (2) |
| O1—Mn2—Cl3 | 88.16 (8) | C21—C20—C9 | 122.8 (2) |
| O1—Mn2—Cl4 | 87.81 (8) | C20—C21—H21 | 120.4 |
| O1—Mn2—N4 | 158.31 (9) | C22—C21—C20 | 119.2 (3) |
| O1—Mn2—N6 | 86.49 (9) | C22—C21—H21 | 120.4 |
| Cl3—Mn2—Cl2 | 80.95 (2) | C21—C22—H22 | 120.2 |
| Cl4—Mn2—Cl2 | 89.05 (3) | C23—C22—C21 | 119.7 (3) |
| Cl4—Mn2—Cl3 | 169.15 (3) | C23—C22—H22 | 120.2 |
| N4—Mn2—Cl2 | 110.53 (5) | C22—C23—H23 | 120.8 |
| N4—Mn2—Cl3 | 92.69 (5) | C22—C23—C24 | 118.5 (3) |
| N4—Mn2—Cl4 | 94.77 (5) | C24—C23—H23 | 120.8 |
| N6—Mn2—Cl2 | 175.19 (6) | N3—C24—C23 | 123.2 (3) |
| N6—Mn2—Cl3 | 94.86 (6) | N3—C24—H24 | 118.4 |
| N6—Mn2—Cl4 | 94.95 (6) | C23—C24—H24 | 118.4 |
| N6—Mn2—N4 | 71.83 (7) | N4—C25—C26 | 118.3 (2) |
| Mn1—Cl2—Mn2 | 93.75 (2) | N4—C25—C30 | 123.3 (2) |
| C34Aa—C35Aa—H35C | 109.5 | C26—C25—C30 | 118.4 (2) |
| C35Bb—C34Bb—H34C | 109.7 | C25—C26—H26 | 119.5 |
| H34Cb—C34Bb—H34D | 108.2 | C27—C26—C25 | 120.9 (2) |
| C35Bb—C34Bb—H34D | 109.7 | C27—C26—H26 | 119.5 |
| C34Bb—C35Bb—H35D | 109.5 | C26—C27—H27 | 118.9 |
| H35Db—C35Bb—H35E | 109.5 | C26—C27—C28 | 122.1 (2) |
| C34Bb—C35Bb—H35E | 109.5 | C28—C27—H27 | 118.9 |
| H35Db—C35Bb—H35F | 109.5 | N5—C28—C27 | 119.8 (2) |
| C34Bb—C35Bb—H35F | 109.5 | N5—C28—C29 | 123.0 (2) |
| H35Eb—C35Bb—H35F | 109.5 | C29—C28—C27 | 117.1 (2) |
| C34Aa—N5—C36 | 116.7 (2) | C28—C29—H29 | 118.9 |
| C4—N2—C10 | 122.0 (3) | C28—C29—C30 | 122.1 (2) |
| C4—N2—C12 | 119.2 (3) | C30—C29—H29 | 118.9 |
| C10—N2—C12 | 116.8 (3) | C25—C30—C31 | 116.8 (2) |
| C1—C2—H2 | 119.3 | C29—C30—C25 | 119.2 (2) |
| C3—C2—C1 | 121.5 (3) | C29—C30—C31 | 124.0 (2) |
| C3—C2—H2 | 119.3 | C30—C31—C38 | 122.7 (2) |
| Mn1—Cl3—Mn2 | 95.97 (3) | C32—C31—C30 | 118.1 (2) |
| C20—N3—Mn1 | 117.72 (16) | C32—C31—C38 | 119.2 (2) |
| C24—N3—Mn1 | 124.00 (19) | C31—C32—H32 | 119.6 |
| C24—N3—C20 | 118.3 (2) | C31—C32—C33 | 120.9 (2) |
| C2—C3—H3 | 119.1 | C33—C32—H32 | 119.6 |
| C2—C3—C4 | 121.8 (3) | N4—C33—C32 | 122.1 (2) |
| C4—C3—H3 | 119.1 | N4—C33—C44 | 116.2 (2) |
| C25—N4—Mn2 | 126.91 (15) | C32—C33—C44 | 121.6 (2) |
| C33—N4—Mn2 | 113.09 (15) | N5—C36—H36A | 108.5 |
| C33—N4—C25 | 118.2 (2) | N5—C36—H36B | 108.5 |

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| N2—C4—C3 | 120.9 (3) | N5—C36—C37 | 115.2 (3) |
| N2—C4—C5 | 121.6 (3) | H36A—C36—H36B | 107.5 |
| C5—C4—C3 | 117.6 (3) | C37—C36—H36A | 108.5 |
| N5—C34Aa—H34A | 109.6 | C37—C36—H36B | 108.5 |
| N5—C34Aa—H34B | 109.6 | C36—C37—H37A | 109.5 |
| N5—C34Aa—C35A | 110.2 (3) | C36—C37—H37B | 109.5 |
| C28—N5—C34A | 121.7 (2) | C36—C37—H37C | 109.5 |
| C28—N5—C34B | 115.0 (11) | H37A—C37—H37B | 109.5 |
| C28—N5—C36 | 121.6 (2) | H37A—C37—H37C | 109.5 |
| C36—N5—C34B | 112.9 (10) | H37B—C37—H37C | 109.5 |
| C4—C5—H5 | 119.1 | C39—C38—C31 | 120.8 (2) |
| C4—C5—C6 | 121.9 (3) | C43—C38—C31 | 120.9 (2) |
| C6—C5—H5 | 119.1 | C43—C38—C39 | 118.1 (2) |
| C44—N6—Mn2 | 115.72 (15) | C38—C39—H39 | 119.6 |
| C48—N6—Mn2 | 125.71 (19) | C40—C39—C38 | 120.8 (3) |
| C48—N6—C44 | 118.5 (2) | C40—C39—H39 | 119.6 |
| C1—C6—C7 | 117.1 (2) | C39—C40—H40 | 119.9 |
| C5—C6—C1 | 119.4 (2) | C41—C40—C39 | 120.1 (3) |
| C5—C6—C7 | 123.5 (2) | C41—C40—H40 | 119.9 |
| C6—C7—C14 | 123.1 (2) | C40—C41—H41 | 120.1 |
| C8—C7—C6 | 117.9 (2) | C40—C41—C42 | 119.9 (3) |
| C8—C7—C14 | 119.0 (2) | C42—C41—H41 | 120.1 |
| C7—C8—H8 | 119.2 | C41—C42—H42 | 119.9 |
| C7—C8—C9 | 121.6 (2) | C41—C42—C43 | 120.3 (3) |
| C9—C8—H8 | 119.2 | C43—C42—H42 | 119.9 |
| N1—C9—C8 | 121.6 (2) | C38—C43—H43 | 119.6 |
| N1—C9—C20 | 117.1 (2) | C42—C43—C38 | 120.8 (3) |
| C8—C9—C20 | 121.3 (2) | C42—C43—H43 | 119.6 |
| N2—C10—H10A | 108.8 | N6—C44—C33 | 116.4 (2) |
| N2—C10—H10B | 108.8 | N6—C44—C45 | 121.5 (2) |
| N2—C10—C11 | 113.6 (3) | C45—C44—C33 | 121.8 (2) |
| H10A—C10—H10B | 107.7 | C44—C45—H45 | 120.4 |
| C11—C10—H10A | 108.8 | C46—C45—C44 | 119.2 (3) |
| C11—C10—H10B | 108.8 | C46—C45—H45 | 120.4 |
| C10—C11—H11A | 109.5 | C45—C46—H46 | 120.3 |
| C10—C11—H11B | 109.5 | C47—C46—C45 | 119.4 (3) |
| C10—C11—H11C | 109.5 | C47—C46—H46 | 120.3 |
| H11A—C11—H11B | 109.5 | C46—C47—H47 | 121.0 |
| H11A—C11—H11C | 109.5 | C46—C47—C48 | 118.1 (3) |
| N5—C34Bb—H34C | 109.7 | C48—C47—H47 | 121.0 |
| N5—C34Bb—H34D | 109.7 | N6—C48—C47 | 123.3 (3) |
| N5—C34Bb—C35B | 109.7 (10) | N6—C48—H48 | 118.4 |
| H11B—C11—H11C | 109.5 | C47—C48—H48 | 118.4 |

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| Mn1—N1—C1—C2 | −12.0 (3) | C15—C14—C19—C18 | 0.0 (5) |
| Mn1—N1—C1—C6 | 167.64 (18) | C15—C16—C17—C18 | −0.2 (7) |
| Mn1—N1—C9—C8 | −169.87 (18) | C16—C17—C18—C19 | 0.5 (6) |
| Mn1—N1—C9—C20 | 8.1 (3) | C17—C18—C19—C14 | −0.4 (5) |

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| Mn1—N3—C20—C9 | 2.2 (3) | C19—C14—C15—C16 | 0.3 (5) |
| Mn1—N3—C20—C21 | −177.6 (2) | C20—N3—C24—C23 | −0.5 (4) |
| Mn1—N3—C24—C23 | 177.8 (2) | C20—C21—C22—C23 | 0.2 (5) |
| N1—C1—C2—C3 | 178.9 (3) | C21—C22—C23—C24 | 0.1 (5) |
| N1—C1—C6—C5 | −179.8 (2) | C22—C23—C24—N3 | 0.0 (5) |
| N1—C1—C6—C7 | 0.6 (4) | C24—N3—C20—C9 | −179.3 (2) |
| N1—C9—C20—N3 | −7.1 (3) | C24—N3—C20—C21 | 0.8 (4) |
| N1—C9—C20—C21 | 172.8 (2) | C25—N4—C33—C32 | 8.8 (3) |
| C1—N1—C9—C8 | 1.0 (4) | C25—N4—C33—C44 | −168.2 (2) |
| C1—N1—C9—C20 | 179.0 (2) | C25—C26—C27—C28 | 0.4 (4) |
| C1—C2—C3—C4 | −0.2 (5) | C25—C30—C31—C32 | 7.1 (3) |
| C1—C6—C7—C8 | 2.2 (4) | C25—C30—C31—C38 | −171.8 (2) |
| C1—C6—C7—C14 | −176.5 (2) | C26—C25—C30—C29 | −2.2 (3) |
| Mn2—N4—C25—C26 | −24.3 (3) | C26—C25—C30—C31 | 179.7 (2) |
| Mn2—N4—C25—C30 | 158.73 (17) | C26—C27—C28—N5 | 175.5 (3) |
| Mn2—N4—C33—C32 | −156.83 (18) | C26—C27—C28—C29 | −2.5 (4) |
| Mn2—N4—C33—C44 | 26.1 (2) | C27—C28—C29—C30 | 2.2 (4) |
| Mn2—N6—C44—C33 | −10.3 (3) | C28—N5—C34Bb—C35Bb | −101.4 (18) |
| Mn2—N6—C44—C45 | 175.29 (19) | C28—N5—C34Aa—C35Aa | 75.9 (4) |
| Mn2—N6—C48—C47 | −176.6 (2) | C28—N5—C36—C37 | −84.6 (4) |
| N2—C4—C5—C6 | 177.2 (3) | C28—C29—C30—C25 | 0.1 (4) |
| C2—C1—C6—C5 | −0.1 (4) | C28—C29—C30—C31 | 178.0 (2) |
| C2—C1—C6—C7 | −179.7 (2) | C29—C30—C31—C32 | −170.8 (2) |
| C2—C3—C4—N2 | −178.1 (3) | C29—C30—C31—C38 | 10.3 (4) |
| C2—C3—C4—C5 | 2.0 (5) | C30—C25—C26—C27 | 2.0 (4) |
| N3—C20—C21—C22 | −0.7 (4) | C30—C31—C32—C33 | −3.5 (3) |
| C3—C4—C5—C6 | −2.9 (4) | C30—C31—C38—C39 | 48.1 (3) |
| N4—C25—C26—C27 | −175.1 (2) | C30—C31—C38—C43 | −137.0 (3) |
| N4—C25—C30—C29 | 174.8 (2) | C31—C32—C33—N4 | −4.8 (4) |
| N4—C25—C30—C31 | −3.3 (3) | C31—C32—C33—C44 | 172.0 (2) |
| N4—C33—C44—N6 | −11.2 (3) | C31—C38—C39—C40 | 174.3 (2) |
| N4—C33—C44—C45 | 163.2 (2) | C31—C38—C43—C42 | −175.6 (3) |
| C4—N2—C10—C11 | 85.2 (4) | C32—C31—C38—C39 | −130.8 (3) |
| C4—N2—C12—C13 | 96.5 (5) | C32—C31—C38—C43 | 44.1 (3) |
| C4—C5—C6—C1 | 2.0 (4) | C32—C33—C44—N6 | 171.7 (2) |
| C4—C5—C6—C7 | −178.4 (3) | C32—C33—C44—C45 | −13.9 (4) |
| N5—C28—C29—C30 | −175.7 (3) | C33—N4—C25—C26 | 172.3 (2) |
| C5—C6—C7—C8 | −177.4 (3) | C33—N4—C25—C30 | −4.7 (3) |
| C5—C6—C7—C14 | 3.9 (4) | C34Aa—N5—C28—C27 | 4.3 (5) |
| N6—C44—C45—C46 | 2.1 (4) | C34Bb—N5—C28—C27 | 41.2 (9) |
| C6—C1—C2—C3 | −0.8 (4) | C34Aa—N5—C28—C29 | −177.9 (3) |
| C6—C7—C8—C9 | −3.4 (4) | C34Bb—N5—C28—C29 | −140.9 (8) |
| C6—C7—C14—C15 | 56.2 (4) | C33—C44—C45—C46 | −172.1 (2) |
| C6—C7—C14—C19 | −130.4 (3) | C36—N5—C34Bb—C35Bb | 112.9 (17) |
| C7—C8—C9—N1 | 1.9 (4) | C36—N5—C34Aa—C35Aa | −103.5 (3) |
| C7—C8—C9—C20 | −176.0 (2) | C36—N5—C28—C27 | −176.4 (3) |
| C7—C14—C15—C16 | 173.8 (3) | C36—N5—C28—C29 | 1.5 (5) |
| C7—C14—C19—C18 | −173.5 (3) | C38—C31—C32—C33 | 175.4 (2) |

| | | | |
|---|---|---|---|
| C8—C7—C14—C15 | −122.5 (3) | C34Aa—N5—C36—C37 | 94.8 (4) |
| C8—C7—C14—C19 | 50.9 (4) | C34Bb—N5—C36—C37 | 58.5 (9) |
| C8—C9—C20—N3 | 170.9 (2) | C38—C39—C40—C41 | 1.2 (4) |
| C8—C9—C20—C21 | −9.2 (4) | C39—C38—C43—C42 | −0.6 (4) |
| C9—N1—C1—C2 | 178.1 (2) | C39—C40—C41—C42 | −0.3 (5) |
| C9—N1—C1—C6 | −2.2 (4) | C40—C41—C42—C43 | −1.0 (5) |
| C9—C20—C21—C22 | 179.4 (3) | C41—C42—C43—C38 | 1.4 (5) |
| C10—N2—C4—C3 | −3.1 (5) | C43—C38—C39—C40 | −0.7 (4) |
| C10—N2—C4—C5 | 176.8 (3) | C44—N6—C48—C47 | −0.1 (4) |
| C10—N2—C12—C13 | −99.2 (4) | C44—C45—C46—C47 | −1.0 (4) |
| C12—N2—C4—C3 | 160.4 (3) | C45—C46—C47—C48 | −0.6 (4) |
| C12—N2—C4—C5 | −19.8 (5) | C46—C47—C48—N6 | 1.2 (5) |
| C12—N2—C10—C11 | −78.6 (4) | C48—N6—C44—C33 | 172.9 (2) |
| C14—C7—C8—C9 | 175.3 (2) | C48—N6—C44—C45 | −1.5 (4) |
| C14—C15—C16—C17 | −0.2 (6) | | |

*Hydrogen-bond geometry (Å, º)*

*Cg1*–*Cg*4 are the centroids of the C1–C6, C38–C43, N3/C20–C24 and C25–C30 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C12—H12*A*···Cl1*B*$^{i}$ | 0.97 | 2.81 | 3.734 (7) | 158 |
| C23—H23···Cl3$^{ii}$ | 0.93 | 2.74 | 3.567 (3) | 149 |
| C45—H45···Cl4$^{iii}$ | 0.93 | 2.69 | 3.563 (3) | 157 |
| C11—H11*A*···*Cg*1$^{i}$ | 0.96 | 2.97 | 3.585 (4) | 123 |
| C21—H21···*Cg*2$^{iv}$ | 0.93 | 2.89 | 3.642 (3) | 139 |
| C36—H36*B*···*Cg*3$^{iv}$ | 0.97 | 2.96 | 3.845 (3) | 153 |
| C35*B*—H35*D*···*Cg*4$^{iv}$ | 0.96 | 2.84 | 3.45 (2) | 122 |

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