# metal-organic compounds

# Poly[[diaquatetrakis(μ2-benzene-1,4-dicarbonitrile-κ2N:N′)iron(II)] bis[tetrachloridoferrate(III)] nitromethane tetrasolvate]

## Pimonrat Prommon, Pinyada Promseenong and Kittipong Chainok*

Department of Chemistry, Faculty of Science, Naresuan University, Muang Phitsanulok 65000, Thailand

Correspondence e-mail: kittipongc@nu.ac.th

In the title compound, $\{[Fe^{II}(C_8H_4N_2)_2(H_2O)_2][Fe^{III}Cl_4]_2\cdot 4CH_3NO_2\}_n$, the $Fe^{II}$ and $Fe^{III}$ ions are hexa- and tetra-coordinated, respectively. Each unique benzene-1,4-dicarbonitrile molecule lies across a crystallographic inversion centre and bridges two $Fe^{II}$ ions (each situated on an inversion centre), generating two-dimensional (4,4) square grid layers. The tetrachloridoferrate(III) anions and nitromethane solvent molecules lie between the square grid layers and are further link to the adjacent layers into a three-dimensional supramolecular structure through O—H···Cl and O—H···O hydrogen bonds.

## Related literature

For background to $Fe^{II}$ spin-crossover complexes, see: Kahn & Martinez (1998); Neville *et al.* (2007, 2008); Murray (2008). For the use of two connecting organodinitrile ligands for the development of magnetism, see: Chainok *et al.* (2010, 2012). For the synthesis, see: Chainok *et al.* (2012).
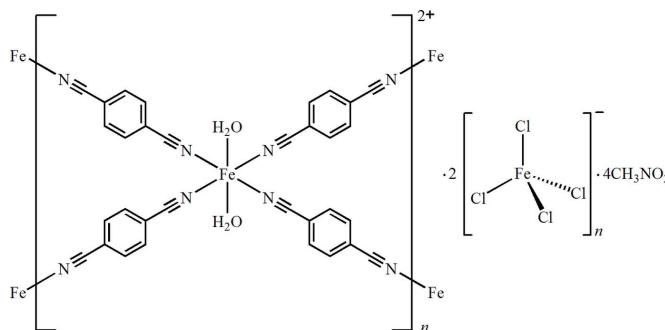


## Experimental

### Crystal data

| | |
|---|---|
| $[Fe(C_8H_4N_2)_2(H_2O)_2][FeCl_4]_2\cdot$ $4CH_3NO_2$ | $\beta = 102.466$ (1)° |
| $M_r = 987.62$ | $V = 1989.9$ (3) Å$^3$ |
| Monoclinic, $P2_1/n$ | $Z = 2$ |
| $a = 12.1307$ (9) Å | Mo $K\alpha$ radiation |
| $b = 12.1554$ (9) Å | $\mu = 1.67$ mm$^{-1}$ |
| $c = 13.8209$ (10) Å | $T = 100$ K |
| | $0.27 \times 0.27 \times 0.24$ mm |

### Data collection

| | |
|---|---|
| Bruker SMART APEX CCD area-detector diffractometer | 11573 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 4397 independent reflections |
| | 3541 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.661$, $T_{max} = 0.690$ | $R_{int} = 0.030$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.073$ | |
| $S = 1.03$ | |
| 4397 reflections | $\Delta\rho_{max} = 0.76$ e Å$^{-3}$ |
| 233 parameters | $\Delta\rho_{min} = -0.50$ e Å$^{-3}$ |
| 3 restraints | |

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

| Fe1—O1 | 2.0884 (15) | Fe2—Cl2 | 2.1811 (6) |
|---|---|---|---|
| Fe1—N21 | 2.1309 (17) | Fe2—Cl3 | 2.1968 (6) |
| Fe1—N11 | 2.1649 (17) | Fe2—Cl4 | 2.1996 (6) |
| Cl1—Fe2 | 2.2070 (6) | | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···O2 | 0.87 (2) | 1.99 (2) | 2.804 (2) | 155 (3) |
| O1—H1···O4 | 0.87 (2) | 2.57 (3) | 3.074 (3) | 118 (2) |
| O1—H2···Cl1 | 0.84 (2) | 2.43 (2) | 3.2731 (16) | 177 (3) |

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

## References

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

# metal-organic compounds

Bruker (2002). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chainok, K., Harding, D. J., Moubaraki, B., Batten, S. R. & Murray, S. R. (2012). Unpublished results.

Chainok, K., Neville, S. M., Moubaraki, B., Batten, S. R., Murray, K. S., Forsyth, C. M., Cashion, J. D. & Haller, K. J. (2010). *Dalton Trans.* **39**, 10900–10909.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Kahn, O. & Martinez, C. J. (1998). *Science*, **279**, 44–48.

Murray, K. S. (2008). *Eur. J. Inorg. Chem.* pp. 3101–3121.

Neville, S. M., Leita, B. A., Halder, G. J., Kepert, C. J., Moubaraki, B., Létard, J.-F. & Murray, K. S. (2008). *Chem. Eur. J.* **14**, 10123–10133.

Neville, S. M., Leita, B. A., Offermann, D. A., Duriska, M. B., Moubaraki, B., Chapman, K. W., Halder, J. D. & Murray, K. S. (2007). *Eur. J. Inorg. Chem.* pp. 1073–1085.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

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

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

**supplementary materials**

# Poly[[diaquatetrakis($\mu_2$-benzene-1,4-dicarbonitrile-$\kappa^2 N$:*N*')iron(II)] bis[tetrachloridoferrate(III)] nitromethane tetrasolvate]

## P. Prommon, P. Promseenong and K. Chainok

## Comment

The $d^6$ Fe(II) complexes exhibiting spin-crossover (SCO) transitions between a $^1A_1$ low spin ($S = 0$) and a $^5T_2$ high spin ($S = 2$) states are of interest due to their possible applications as molecular switches or materials for information storage (Kahn & Martinez 1998). Although the fundamental origin of the SCO phenomenon is molecular, SCO transitions in the crystal structure can be reversibly switched by external stimuli such as light, temperature and pressure as well as the existence of long or short range supramolecular interactions (Neville *et al.* 2007, 2008; Murray 2008). The title compound was obtained as a minor product in another an earlier from part of further study of how the nature of the two-connecting organodinitrile bridging ligands affect the SCO phenomenon in the Fe(II) complexes (Chainok *et al.* 2010).

A fragment containing the asymmetric unit with atom numbering and coordination environments of the metal centre of the title compound is shown in Fig. 1. The asymmetric unit contains one iron(II) cation (half-occupancy), one coordinated water molecule, half of two independent benzene-1,4-dicarbonitrile ligand, one tetrachloridoferrate(III) anion, and two nitromethane solvent molecules. The Fe$^{II}$ ion resides in an inversion center and is octahedrally coordinated by four nitrogen atoms from benzene-1,4-dicarbonitrile ligands in the equatorial plane and two equivalent terminal water molecules occupying the axial positions. The Fe—N and Fe—O bond lengths in the title compound, Table 1, are comparable to that observed for a high spin species in the corresponding Fe(II) complex containing the two-connecting organodinitrile ligands such as [Fe$^{II}$(AIBN)(H$_2$O)][Fe$^{III}$Cl$_4$]$_2$ (Fe—N = 2.144 (1)–2.171 (1) Å and Fe–O = 2.084 (1) Å), AIBN = 2,2'-azobisisobutyronitrile (Chainok *et al.* 2010). Each benzene-1,4-dicarbonitrile ligand has crystallographically imposed inversion symmetry and is bound to two neighboring Fe$^{II}$ ions generating two-dimensional approximate square grid layers with (4,4) topology perpendicular to the *c* axis, with the dimension of 12.1307 (9) × 12.1554 (9) Å (Fe$^{II}$···Fe$^{II}$ distances across the benzene-1,4-dicarbonitrile ligand), Fig. 2. The layers are packed to each other with an interlayer separation of 6.0777 (5) Å.

The Fe$^{III}$ atom is a tetrahedrally coordinated to four chloride anions. The bond lengths and angles around the Fe(III) ions are within the common ranges for this type of coordination environment (Chainok *et al.* 2010). The tetrachloridoferrate(III) anions and the nitromethane solvent molecules all lie in general position in the structure, and are included in the layers by eschewing the interpenetration of the networks. These guest molecules are then further linked to the adjacent two-dimensional layers into a three-dimensional supramolecular structure through O—H···Cl and O—H···O hydrogen bonds formed between the apically water molecules coordinated to the metal ions and Cl and O atoms of the guest molecules, Table 2.

## Experimental

Single crystals of the title compound were obtained as the minor product during the synthesis of [Fe$^{II}$(C$_8$H$_4$N$_2$)$_2$][Fe$^{III}$Cl$_4$]$_2$ (Chainok *et al.* 2012) when traces of air and moisture are presented. Typically, FeCl$_2$ (62 mg, 0.5 mmol) and FeCl$_3$ (163

mg, 1 mmol) were dissolved in 3 ml of $CH_3NO_2$ to formed a yellow brown solution and this was pipetted into one side of the H-tube. Benzene-1,4-dicarbonitrile (192 mg, 1.5 mmol) was dissolved in 3 ml of $CH_3NO_2$ to give a colorless solution and this was pipetted into the other side arm of the H-tube. The H-tube was then carefully filled with $CH_3NO_2$. Upon slow diffusion for two weeks, yellow block-shaped of the major product (*ca*. 60% yield based on $FeCl_2$) and pale yellow plate of the minor product (*ca*. 5% yield based on $FeCl_2$) single crystals were formed in the iron-containing side of the H-tube.

### Refinement

The hydrogen atoms were placed in the geometrically idealized positions and constrained to ride on their parent atom positions with a C–H distances of 0.95 and 0.99 Å $U_{iso}(H) = 1.2U_{eq}(C)$ and 0.98 Å for $CH_3$ [$U_{iso}(H) = 1.5U_{eq}(C)$]. The hydrogen atoms attached to oxygen atoms of the water molecules were located in a difference Fourier map and refined being in their as-found positions with a *DFIX* restraint of O—H distance at 0.90 Å, with $U_{iso}(H) = 1.2U_{eq}(O)$.

### Figures
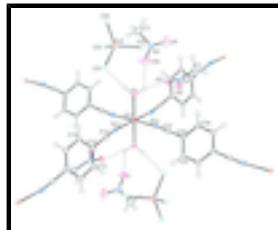


Fig. 1. Displacement ellipsoid plot of a fragment at the 50% probability level containing the asymmetric unit with atom numbering and coordination environments of the metal centers of the title compound.
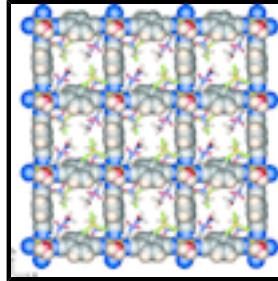


Fig. 2. Inclusion of tetrachloridoferrate(III) anions and nitromethane molecules in the square grid networks of the title compound.

**Poly[[diaquatetrakis(µ$_2$-benzene-1,4-dicarbonitrile- κ$^2$N:N')iron(II)] bis[tetrachloroferrate(III)] nitromethane tetrasolvate]**

*Crystal data*

| | |
|---|---|
| [Fe(C$_8$H$_4$N$_2$)$_2$(H$_2$O)$_2$][FeCl$_4$]$_2$·4CH$_3$NO$_2$ | $F(000) = 988$ |
| $M_r = 987.62$ | $D_x = 1.648$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2yn | Cell parameters from 3583 reflections |
| $a = 12.1307$ (9) Å | $\theta = 2.4–27.4°$ |
| $b = 12.1554$ (9) Å | $\mu = 1.67$ mm$^{-1}$ |
| $c = 13.8209$ (10) Å | $T = 100$ K |
| $\beta = 102.466$ (1)° | Block, yellow |
| $V = 1989.9$ (3) Å$^3$ | $0.27 \times 0.27 \times 0.24$ mm |

$Z = 2$

*Data collection*

| | |
|---|---|
| Bruker SMART APEX CCD area-detector diffractometer | 4397 independent reflections |
| Radiation source: fine-focus sealed tube | 3541 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.030$ |
| Detector resolution: 8 pixels mm$^{-1}$ | $\theta_{max} = 28.1°$, $\theta_{min} = 2.0°$ |
| $\omega$ and $\varphi$ scans | $h = -15\rightarrow16$ |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | $k = -12\rightarrow15$ |
| $T_{min} = 0.661$, $T_{max} = 0.690$ | $l = -17\rightarrow17$ |
| 11573 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.073$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.03$ | $w = 1/[\sigma^2(F_o^2) + (0.042P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 4397 reflections | $(\Delta/\sigma)_{max} = 0.001$ |
| 233 parameters | $\Delta\rho_{max} = 0.76$ e Å$^{-3}$ |
| 3 restraints | $\Delta\rho_{min} = -0.50$ 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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| Fe1 | 0.5000 | 0.5000 | 0.5000 | 0.01056 (10) |
| Cl1 | 0.31456 (5) | 0.45491 (4) | 0.76369 (4) | 0.02217 (13) |
| O1 | 0.52584 (13) | 0.46637 (12) | 0.65141 (11) | 0.0173 (3) |
| N1 | 0.74782 (15) | 0.26095 (15) | 0.71549 (13) | 0.0200 (4) |

| | | | | |
|---|---|---|---|---|
| C1 | 0.7964 (2) | 0.15057 (19) | 0.74355 (17) | 0.0270 (5) |
| H1A | 0.7828 | 0.1301 | 0.8086 | 0.040* |
| H1B | 0.8778 | 0.1522 | 0.7465 | 0.040* |
| H1C | 0.7606 | 0.0965 | 0.6941 | 0.040* |
| H1 | 0.576 (2) | 0.417 (2) | 0.676 (2) | 0.052 (9)* |
| Fe2 | 0.29049 (3) | 0.29511 (2) | 0.83208 (2) | 0.01702 (9) |
| Cl2 | 0.42489 (5) | 0.18565 (5) | 0.80885 (4) | 0.02811 (14) |
| O2 | 0.64553 (13) | 0.26786 (12) | 0.68614 (12) | 0.0259 (4) |
| N2 | 0.67018 (18) | 0.34984 (17) | 0.93557 (15) | 0.0297 (5) |
| C2 | 0.6206 (3) | 0.3774 (2) | 1.0194 (2) | 0.0437 (7) |
| H2A | 0.6721 | 0.3550 | 1.0810 | 0.066* |
| H2B | 0.5485 | 0.3388 | 1.0131 | 0.066* |
| H2C | 0.6080 | 0.4570 | 1.0205 | 0.066* |
| H2 | 0.4716 (18) | 0.466 (2) | 0.6803 (19) | 0.043 (9)* |
| Cl3 | 0.12062 (5) | 0.23479 (4) | 0.76444 (4) | 0.02225 (13) |
| O3 | 0.81115 (14) | 0.33973 (14) | 0.72375 (13) | 0.0318 (4) |
| Cl4 | 0.30172 (5) | 0.31921 (5) | 0.99164 (4) | 0.02609 (14) |
| O4 | 0.6489 (2) | 0.41206 (17) | 0.86466 (15) | 0.0661 (7) |
| O5 | 0.72545 (17) | 0.26586 (17) | 0.93885 (17) | 0.0515 (6) |
| N11 | 0.49078 (14) | 0.32436 (14) | 0.47352 (13) | 0.0159 (4) |
| C11 | 0.49325 (17) | 0.23044 (17) | 0.47862 (15) | 0.0151 (4) |
| C12 | 0.49595 (17) | 0.11201 (16) | 0.48873 (15) | 0.0164 (4) |
| C13 | 0.48332 (19) | 0.06644 (17) | 0.57797 (16) | 0.0203 (5) |
| H13 | 0.4724 | 0.1125 | 0.6306 | 0.024* |
| C14 | 0.51318 (19) | 0.04656 (17) | 0.41060 (16) | 0.0200 (5) |
| H14 | 0.5224 | 0.0791 | 0.3503 | 0.024* |
| N21 | 0.32197 (14) | 0.50641 (13) | 0.48775 (13) | 0.0166 (4) |
| C21 | 0.22841 (17) | 0.50554 (16) | 0.48975 (15) | 0.0148 (4) |
| C22 | 0.11031 (17) | 0.50257 (16) | 0.49328 (15) | 0.0146 (4) |
| C23 | 0.07732 (17) | 0.42932 (16) | 0.55939 (15) | 0.0160 (4) |
| H23 | 0.1310 | 0.3821 | 0.5994 | 0.019* |
| C24 | 0.03464 (17) | 0.57343 (17) | 0.43427 (15) | 0.0164 (4) |
| H24 | 0.0595 | 0.6230 | 0.3903 | 0.020* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Fe1 | 0.0092 (2) | 0.00766 (19) | 0.0156 (2) | 0.00009 (14) | 0.00442 (15) | 0.00041 (15) |
| Cl1 | 0.0274 (3) | 0.0176 (3) | 0.0228 (3) | −0.0022 (2) | 0.0083 (2) | 0.0030 (2) |
| O1 | 0.0169 (8) | 0.0178 (8) | 0.0186 (8) | 0.0021 (6) | 0.0067 (6) | 0.0021 (6) |
| N1 | 0.0243 (11) | 0.0234 (10) | 0.0130 (9) | 0.0027 (8) | 0.0053 (8) | 0.0015 (7) |
| C1 | 0.0316 (14) | 0.0252 (13) | 0.0236 (12) | 0.0121 (10) | 0.0046 (10) | 0.0056 (10) |
| Fe2 | 0.02082 (17) | 0.01520 (16) | 0.01655 (17) | 0.00175 (12) | 0.00737 (13) | 0.00109 (12) |
| Cl2 | 0.0319 (3) | 0.0281 (3) | 0.0275 (3) | 0.0120 (2) | 0.0134 (3) | 0.0028 (2) |
| O2 | 0.0192 (8) | 0.0229 (8) | 0.0328 (9) | 0.0043 (6) | −0.0009 (7) | −0.0019 (7) |
| N2 | 0.0383 (13) | 0.0251 (11) | 0.0270 (11) | −0.0068 (9) | 0.0104 (9) | −0.0065 (9) |
| C2 | 0.072 (2) | 0.0264 (14) | 0.0435 (17) | 0.0025 (13) | 0.0369 (16) | −0.0013 (12) |
| Cl3 | 0.0246 (3) | 0.0183 (3) | 0.0254 (3) | −0.0026 (2) | 0.0088 (2) | −0.0022 (2) |

| | | | | | |
|---|---|---|---|---|---|
| O3 | 0.0274 (10) | 0.0317 (10) | 0.0394 (10) | −0.0080 (7) | 0.0139 (8) | −0.0008 (8) |
| Cl4 | 0.0343 (3) | 0.0283 (3) | 0.0175 (3) | 0.0041 (2) | 0.0098 (2) | 0.0008 (2) |
| O4 | 0.132 (2) | 0.0412 (13) | 0.0303 (11) | −0.0064 (13) | 0.0280 (13) | 0.0054 (10) |
| O5 | 0.0399 (12) | 0.0445 (12) | 0.0723 (15) | 0.0128 (9) | 0.0172 (11) | −0.0088 (11) |
| N11 | 0.0160 (9) | 0.0117 (9) | 0.0203 (9) | −0.0003 (6) | 0.0046 (7) | −0.0003 (7) |
| C11 | 0.0140 (10) | 0.0146 (11) | 0.0176 (10) | −0.0011 (8) | 0.0055 (8) | −0.0002 (8) |
| C12 | 0.0167 (10) | 0.0095 (9) | 0.0228 (11) | −0.0021 (8) | 0.0041 (9) | −0.0010 (8) |
| C13 | 0.0283 (12) | 0.0125 (10) | 0.0219 (11) | −0.0007 (8) | 0.0097 (9) | −0.0039 (9) |
| C14 | 0.0285 (12) | 0.0131 (10) | 0.0197 (11) | −0.0022 (9) | 0.0081 (9) | 0.0017 (9) |
| N21 | 0.0145 (9) | 0.0137 (9) | 0.0223 (9) | −0.0001 (7) | 0.0058 (7) | −0.0005 (7) |
| C21 | 0.0165 (11) | 0.0118 (10) | 0.0169 (10) | 0.0000 (8) | 0.0053 (8) | −0.0001 (8) |
| C22 | 0.0109 (9) | 0.0154 (10) | 0.0186 (10) | −0.0018 (7) | 0.0054 (8) | −0.0041 (8) |
| C23 | 0.0147 (10) | 0.0149 (10) | 0.0178 (10) | 0.0018 (8) | 0.0018 (8) | −0.0010 (8) |
| C24 | 0.0157 (10) | 0.0151 (10) | 0.0198 (11) | −0.0022 (8) | 0.0071 (9) | −0.0003 (8) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Fe1—O1 | 2.0884 (15) | N2—C2 | 1.455 (3) |
| Fe1—O1$^i$ | 2.0884 (15) | C2—H2A | 0.9800 |
| Fe1—N21$^i$ | 2.1309 (17) | C2—H2B | 0.9800 |
| Fe1—N21 | 2.1309 (17) | C2—H2C | 0.9800 |
| Fe1—N11 | 2.1649 (17) | N11—C11 | 1.144 (3) |
| Fe1—N11$^i$ | 2.1649 (17) | C11—C12 | 1.446 (3) |
| Cl1—Fe2 | 2.2070 (6) | C12—C13 | 1.390 (3) |
| O1—H1 | 0.872 (17) | C12—C14 | 1.393 (3) |
| O1—H2 | 0.840 (16) | C13—C14$^{ii}$ | 1.382 (3) |
| N1—O3 | 1.218 (2) | C13—H13 | 0.9500 |
| N1—O2 | 1.222 (2) | C14—C13$^{ii}$ | 1.382 (3) |
| N1—C1 | 1.483 (3) | C14—H14 | 0.9500 |
| C1—H1A | 0.9800 | N21—C21 | 1.141 (3) |
| C1—H1B | 0.9800 | C21—C22 | 1.444 (3) |
| C1—H1C | 0.9800 | C22—C24 | 1.388 (3) |
| Fe2—Cl2 | 2.1811 (6) | C22—C23 | 1.395 (3) |
| Fe2—Cl3 | 2.1968 (6) | C23—C24$^{iii}$ | 1.380 (3) |
| Fe2—Cl4 | 2.1996 (6) | C23—H23 | 0.9500 |
| N2—O5 | 1.217 (3) | C24—C23$^{iii}$ | 1.380 (3) |
| N2—O4 | 1.221 (3) | C24—H24 | 0.9500 |
| O1—Fe1—O1$^i$ | 180.0 | Cl4—Fe2—Cl1 | 109.08 (2) |
| O1—Fe1—N21$^i$ | 89.02 (6) | O5—N2—O4 | 124.7 (2) |
| O1$^i$—Fe1—N21$^i$ | 90.98 (6) | O5—N2—C2 | 118.9 (2) |
| O1—Fe1—N21 | 90.98 (6) | O4—N2—C2 | 116.4 (2) |
| O1$^i$—Fe1—N21 | 89.02 (6) | N2—C2—H2A | 109.5 |
| N21$^i$—Fe1—N21 | 180.00 (9) | N2—C2—H2B | 109.5 |
| O1—Fe1—N11 | 88.13 (6) | H2A—C2—H2B | 109.5 |
| O1$^i$—Fe1—N11 | 91.87 (6) | N2—C2—H2C | 109.5 |
| N21$^i$—Fe1—N11 | 89.53 (6) | H2A—C2—H2C | 109.5 |

| | | | |
|---|---|---|---|
| N21—Fe1—N11 | 90.47 (6) | H2B—C2—H2C | 109.5 |
| O1—Fe1—N11$^i$ | 91.87 (6) | C11—N11—Fe1 | 166.95 (17) |
| O1$^i$—Fe1—N11$^i$ | 88.13 (6) | N11—C11—C12 | 177.9 (2) |
| N21$^i$—Fe1—N11$^i$ | 90.47 (6) | C13—C12—C14 | 121.59 (19) |
| N21—Fe1—N11$^i$ | 89.53 (6) | C13—C12—C11 | 118.55 (19) |
| N11—Fe1—N11$^i$ | 180.0 | C14—C12—C11 | 119.85 (19) |
| Fe1—O1—H1 | 118.0 (19) | C14$^{ii}$—C13—C12 | 119.4 (2) |
| Fe1—O1—H2 | 120.9 (19) | C14$^{ii}$—C13—H13 | 120.3 |
| H1—O1—H2 | 111 (2) | C12—C13—H13 | 120.3 |
| O3—N1—O2 | 123.50 (19) | C13$^{ii}$—C14—C12 | 119.0 (2) |
| O3—N1—C1 | 118.69 (19) | C13$^{ii}$—C14—H14 | 120.5 |
| O2—N1—C1 | 117.81 (18) | C12—C14—H14 | 120.5 |
| N1—C1—H1A | 109.5 | C21—N21—Fe1 | 173.63 (17) |
| N1—C1—H1B | 109.5 | N21—C21—C22 | 179.0 (2) |
| H1A—C1—H1B | 109.5 | C24—C22—C23 | 122.29 (19) |
| N1—C1—H1C | 109.5 | C24—C22—C21 | 119.98 (19) |
| H1A—C1—H1C | 109.5 | C23—C22—C21 | 117.71 (18) |
| H1B—C1—H1C | 109.5 | C24$^{iii}$—C23—C22 | 118.85 (19) |
| Cl2—Fe2—Cl3 | 113.33 (3) | C24$^{iii}$—C23—H23 | 120.6 |
| Cl2—Fe2—Cl4 | 110.02 (2) | C22—C23—H23 | 120.6 |
| Cl3—Fe2—Cl4 | 108.69 (2) | C23$^{iii}$—C24—C22 | 118.86 (19) |
| Cl2—Fe2—Cl1 | 107.56 (2) | C23$^{iii}$—C24—H24 | 120.6 |
| Cl3—Fe2—Cl1 | 108.07 (2) | C22—C24—H24 | 120.6 |
| O1—Fe1—N11—C11 | −10.8 (7) | O1—Fe1—N21—C21 | −13.1 (15) |
| O1$^i$—Fe1—N11—C11 | 169.2 (7) | O1$^i$—Fe1—N21—C21 | 166.9 (15) |
| N21$^i$—Fe1—N11—C11 | 78.2 (7) | N21$^i$—Fe1—N21—C21 | 141 (2) |
| N21—Fe1—N11—C11 | −101.8 (7) | N11—Fe1—N21—C21 | 75.1 (15) |
| N11$^i$—Fe1—N11—C11 | −43 (18) | N11$^i$—Fe1—N21—C21 | −104.9 (15) |
| Fe1—N11—C11—C12 | 25 (7) | Fe1—N21—C21—C22 | −35 (15) |
| N11—C11—C12—C13 | 2 (6) | N21—C21—C22—C24 | −168 (13) |
| N11—C11—C12—C14 | −177 (100) | N21—C21—C22—C23 | 14 (14) |
| C14—C12—C13—C14$^{ii}$ | −0.6 (4) | C24—C22—C23—C24$^{iii}$ | 0.6 (3) |
| C11—C12—C13—C14$^{ii}$ | −179.35 (19) | C21—C22—C23—C24$^{iii}$ | 178.61 (18) |
| C13—C12—C14—C13$^{ii}$ | 0.6 (4) | C23—C22—C24—C23$^{iii}$ | −0.6 (3) |
| C11—C12—C14—C13$^{ii}$ | 179.33 (19) | C21—C22—C24—C23$^{iii}$ | −178.57 (18) |

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

*Hydrogen-bond geometry (Å, °)*

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O1—H1···O2 | 0.87 (2) | 1.99 (2) | 2.804 (2) | 155 (3) |
| O1—H1···O4 | 0.87 (2) | 2.57 (3) | 3.074 (3) | 118 (2) |
| O1—H2···Cl1 | 0.84 (2) | 2.43 (2) | 3.2731 (16) | 177 (3) |

**Fig. 1**

**Fig. 2**