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4,4'-(Ethene-1,2-diyl)dipyridinium 4-[2-(pyridin-4-yl)ethenyl]pyridinium octacyanomolybdate(V) tetrahydrate

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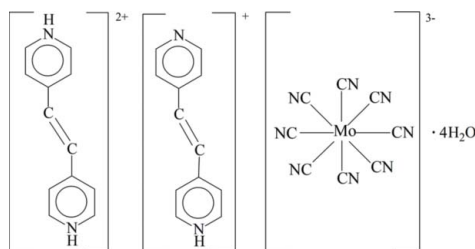
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.021; wR factor = 0.052; data-to-parameter ratio = 12.9.

The crystal structure of the title compound, $(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{C}_{12}\text{H}_{11}\text{N}_2)[\text{Mo}(\text{CN})_8]\cdot 4\text{H}_2\text{O}$, consists of 4,4'-(ethene-1,2-diyl)dipyridinium and 4-[2-(pyridin-4-yl)ethenyl]pyridinium cations disordered over the same site, an $[\text{Mo}(\text{CN})_8]^{3-}$ anion and four water molecules of crystallization. The eight-coordinate $[\text{Mo}(\text{CN})_8]^{3-}$ unit exhibits a slightly distorted square-antiprismatic geometry. In the structure, the cations (crystallographic symmetry, 2) and anions (crystallographic symmetry, 222) are arranged alternately by $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds, forming layers parallel to the bc plane. These layers are further linked through $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds, generating a three-dimensional supra-molecular network.

Related literature

For general background to the design and construction of multi-functional materials, see: Nowicka *et al.* (2012); Prins *et al.* (2007); Sieklucka *et al.* (2011); Tanase *et al.* (2008); Zhou *et al.* (2012). For related structures, see: Liu *et al.* (2008); Qian *et al.* (2009).



Experimental

Crystal data

$(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{C}_{12}\text{H}_{11}\text{N}_2)[\text{Mo}(\text{CN})_8]\cdot 4\text{H}_2\text{O}$
 $V = 3151.8$ (11) Å³
 $Z = 4$
 $M_r = 743.63$
 Orthorhombic, *Ccca*
 $a = 12.403$ (3) Å
 $b = 16.534$ (3) Å
 $c = 15.370$ (3) Å
 Mo $K\alpha$ radiation
 $\mu = 0.48$ mm⁻¹
 $T = 291$ K
 $0.18 \times 0.15 \times 0.13$ mm

Data collection

Bruker SMART APEXII diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
 $T_{\min} = 0.919$, $T_{\max} = 0.941$
 6789 measured reflections
 1442 independent reflections
 1388 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.052$
 $S = 1.09$
 1442 reflections
 112 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1A}\cdots\text{N1}^{\text{i}}$	0.85	2.11	2.9524 (19)	174
$\text{O1}-\text{H1B}\cdots\text{N2}^{\text{ii}}$	0.85	2.00	2.8195 (18)	162
$\text{N3}-\text{H3X}\cdots\text{O1}$	0.89	1.86	2.7342 (17)	166

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ5039).

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supporting information

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4,4'-(Ethene-1,2-diyl)dipyridinium 4-[2-(pyridin-4-yl)ethenyl]pyridinium octacyanidomolybdate(V) tetrahydrate

Xiao-Zhen Yang, Ai-Yun Hu and Ai-Hua Yuan

S1. Comment

In the past few years, much attention has been put into the design and construction of multi-functional materials (Zhou *et al.*, 2012). Octacyanometallates $[M(\text{CN})_8]^{n-}$ ($M = \text{Mo}, \text{W}; n = 3, 4$) with flexible coordination modes and lower symmetries have been aggressively studied recently (Nowicka *et al.*, 2012), because these building blocks can adopt various geometries, *e.g.*, square antiprismatic, dodecahedral or bicapped trigonal prismatic, depending on the external environments. The combination of the $[M(\text{CN})_8]^{n-}$ precursors and the second metal centers has produced various dimensional molecular structures and the resulting materials have displayed intriguing properties (Sieklucka *et al.*, 2011). However, the development of octacyano- and lanthanide-based assemblies has been somewhat hampered by the tendency of the lanthanide ions to adopt higher coordination numbers, their ability to easily adapt to a given environment, and in the absence of design strategies for 4f-4d/5d networks. Recently, we used $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ as building block to react with the lanthanide ion Ce^{3+} and dpe ligand (dpe = 1,2-di(pyridin-4-yl)ethylene), in order to obtain new octacyanide-based 4f/4d compound with open structure. Unfortunately, a new ion-pair compound without Ce^{3+} ions was isolated. The asymmetric unit of the title compound contains 4,4'-ethene-1,2-diyl dipyridinium, $[\text{H}_2\text{dpe}]^{2+}$, and 4-(2-(pyridin-4-yl)ethenyl)pyridinium, $[\text{Hdpe}]^+$, cations, one $[\text{Mo}(\text{CN})_8]^{3-}$ anion, and four crystallized water molecules (Fig. 1). Both the $[\text{H}_2\text{dpe}]^{2+}$ and $[\text{Hdpe}]^+$ cations are disordered over the same site. The eight-coordinated $[\text{Mo}(\text{CN})_8]$ unit exhibits a distorted slightly square antiprismatic geometry, typical of octacyanometallates (Prins *et al.*, 2007; Tanase *et al.*, 2008). The average distances of Mo1—C and C—N bonds are 2.1682 and 1.156 Å, respectively, while the Mo1—CN bonds are almost linear with the maximum deviation from linearity of 3.8°.

In the structure, $[\text{H}_2\text{dpe}]^{2+}$ cation, $[\text{Hdpe}]^+$ cation and $[\text{Mo}(\text{CN})_8]^{3-}$ unit are arranged alternatively through $\text{N3} \cdots \text{H3X} \cdots \text{O1}$ and $\text{O1} \cdots \text{H1B} \cdots \text{N2}^{\text{v}}$ (symmetric code: (v) $-x + 1/2, -y, z$) hydrogen bonds (Table 1) to generate a two-dimensional layer. These layers are further interlinked through $\text{O1} \cdots \text{H1A} \cdots \text{N1}^{\text{iv}}$ (symmetric code: (iv) $x + 1, y - 1/2, -z$) hydrogen bonds, forming a three-dimensional supramolecular network (Fig. 2). This structural feature has also been observed in related octacyanide-based compounds $(\text{C}_{10}\text{H}_{10}\text{N}_4)(\text{C}_{10}\text{H}_9\text{N}_4)[\text{M}(\text{CN})_8] \cdot n\text{H}_2\text{O}$ ($M = \text{Mo}, \text{W}$) (Qian *et al.*, 2009; Liu *et al.*, 2008).

S2. Experimental

Single crystals of the title compound were prepared at room temperature by slow diffusion of a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 *v/v*) solution containing both $\text{Ce}^{\text{III}}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.05 mmol) and dpe (0.15 mmol) in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 *v/v*) solution of $[\text{HN}(n\text{-C}_4\text{H}_9)_3]_3[\text{Mo}^{\text{V}}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ (0.05 mmol). After four weeks, dark-blue rod-like crystals were obtained.

S3. Refinement

All non-H atoms were refined anisotropically. The (C)H atoms were calculated at idealized positions and included in the refinement in a riding mode. The (N)H and (O)H atoms of water molecules were located from a difference Fourier map and refined as riding [$N-H = 0.89 \text{ \AA}$, $U(H) = 1.2U_{eq}(N)$; $O-H = 0.85 \text{ \AA}$, $U(H) = 1.5U_{eq}(O)$], with the occupancy factor of the N-bound H atoms set to 0.75

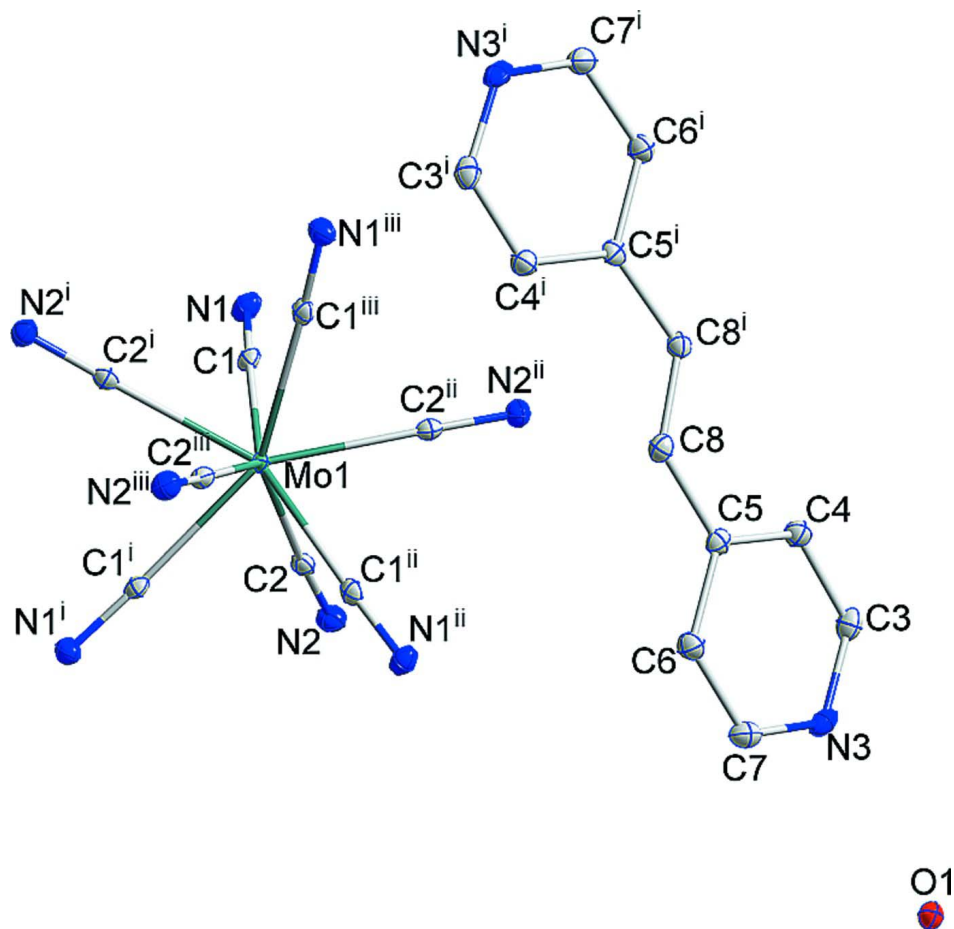
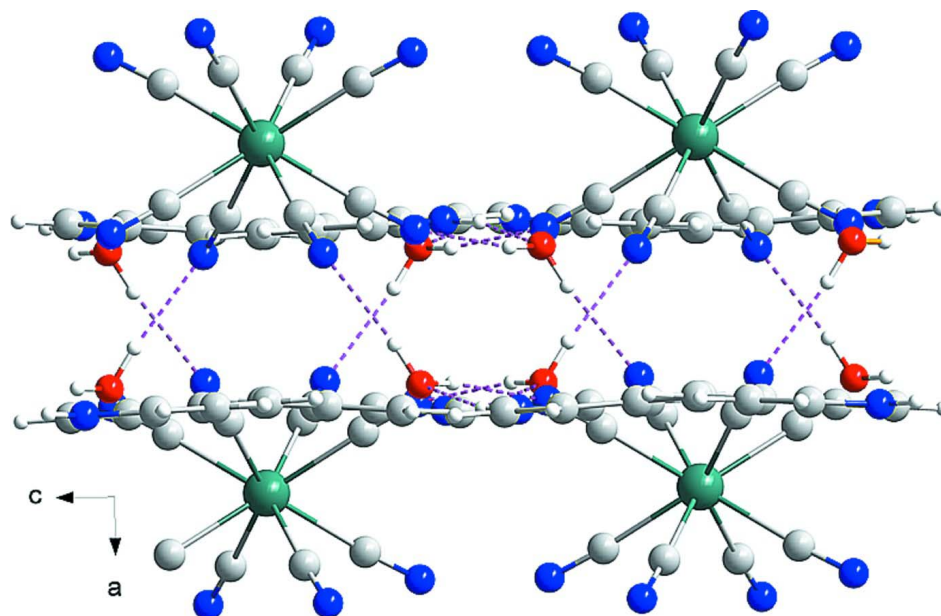


Figure 1

The molecular structure of the title compound with thermal ellipsoids at the 30% probability level. All H atoms were removed for clarity. Symmetry codes: (i) $x, -y + 1/2, -z + 1/2$; (ii) $-x, -y + 1/2, z$; (iii) $-x, y, -z + 1/2$

**Figure 2**

The three-dimensional supramolecular network of the title compound.

4,4'-(Ethene-1,2-diyl)dipyridinium 4-[2-(pyridin-4-yl)ethenyl]pyridinium octacyanomolybdate(V) tetrahydrate

Crystal data

$(C_{12}H_{12}N_2)(C_{12}H_{11}N_2)[Mo(CN)_8] \cdot 4H_2O$

$M_r = 743.63$

Orthorhombic, *Ccca*

Hall symbol: -C 2b 2bc

$a = 12.403 (3) \text{ \AA}$

$b = 16.534 (3) \text{ \AA}$

$c = 15.370 (3) \text{ \AA}$

$V = 3151.8 (11) \text{ \AA}^3$

$Z = 4$

$F(000) = 1524$

$D_x = 1.567 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6602 reflections

$\theta = 3.4\text{--}29.0^\circ$

$\mu = 0.48 \text{ mm}^{-1}$

$T = 291 \text{ K}$

Rod, dark blue

$0.18 \times 0.15 \times 0.13 \text{ mm}$

Data collection

Bruker SMART APEXII
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2004)

$T_{\min} = 0.919$, $T_{\max} = 0.941$

6789 measured reflections

1442 independent reflections

1388 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 25.3^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -14 \rightarrow 14$

$k = -15 \rightarrow 19$

$l = -18 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.052$

$S = 1.09$

1442 reflections

112 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
 $w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 4.1639P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mo1	0.0000	0.2500	0.2500	0.01026 (10)	
O1	0.65008 (10)	-0.07739 (7)	-0.07004 (7)	0.0222 (3)	
H1A	0.7081	-0.0819	-0.0991	0.033*	
H1B	0.6515	-0.1156	-0.0330	0.033*	
N1	-0.15776 (12)	0.39926 (8)	0.18061 (8)	0.0217 (3)	
N2	-0.12604 (11)	0.18087 (8)	0.07447 (9)	0.0214 (3)	
N3	0.61502 (11)	0.04861 (9)	0.04165 (9)	0.0222 (3)	
H3X	0.6177	0.0114	-0.0001	0.027*	0.75
C1	-0.10315 (12)	0.34816 (9)	0.20714 (9)	0.0153 (3)	
C2	-0.08556 (13)	0.20481 (9)	0.13705 (10)	0.0153 (3)	
C3	0.61146 (13)	0.12818 (10)	0.02559 (10)	0.0226 (4)	
H3	0.6063	0.1466	-0.0314	0.027*	
C4	0.61534 (13)	0.18237 (10)	0.09245 (10)	0.0197 (3)	
H4	0.6125	0.2375	0.0809	0.024*	
C5	0.62366 (12)	0.15508 (9)	0.17825 (10)	0.0171 (3)	
C6	0.62332 (13)	0.07142 (10)	0.19249 (11)	0.0212 (4)	
H6	0.6258	0.0511	0.2489	0.025*	
C7	0.61929 (14)	0.01956 (10)	0.12305 (11)	0.0239 (4)	
H7	0.6195	-0.0360	0.1324	0.029*	
C8	0.62950 (13)	0.20979 (10)	0.25268 (10)	0.0177 (3)	
H8	0.6335	0.1868	0.3078	0.021*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.01259 (15)	0.00997 (14)	0.00822 (14)	0.000	0.000	0.000
O1	0.0281 (6)	0.0209 (6)	0.0175 (6)	0.0004 (5)	0.0046 (5)	-0.0005 (5)
N1	0.0279 (8)	0.0213 (7)	0.0158 (7)	0.0060 (6)	-0.0014 (6)	-0.0007 (6)
N2	0.0263 (8)	0.0205 (7)	0.0175 (7)	-0.0032 (6)	-0.0032 (6)	-0.0003 (6)
N3	0.0209 (7)	0.0244 (8)	0.0213 (7)	0.0016 (6)	0.0000 (6)	-0.0098 (6)
C1	0.0185 (8)	0.0168 (8)	0.0107 (7)	-0.0012 (6)	0.0010 (6)	-0.0029 (6)
C2	0.0168 (8)	0.0125 (8)	0.0166 (8)	-0.0007 (6)	0.0011 (7)	0.0027 (6)

C3	0.0219 (8)	0.0295 (10)	0.0164 (8)	0.0023 (7)	0.0000 (7)	-0.0004 (7)
C4	0.0222 (8)	0.0181 (8)	0.0188 (8)	0.0018 (6)	0.0005 (7)	0.0007 (6)
C5	0.0141 (7)	0.0187 (8)	0.0186 (8)	0.0013 (6)	0.0003 (6)	-0.0010 (6)
C6	0.0253 (9)	0.0193 (8)	0.0190 (8)	0.0005 (7)	-0.0006 (7)	0.0013 (6)
C7	0.0255 (9)	0.0182 (9)	0.0281 (9)	0.0005 (7)	-0.0011 (8)	-0.0028 (7)
C8	0.0184 (8)	0.0199 (8)	0.0149 (8)	0.0019 (7)	-0.0011 (6)	0.0002 (6)

Geometric parameters (Å, °)

Mo1—C2	2.1674 (16)	N3—C7	1.341 (2)
Mo1—C2 ⁱ	2.1674 (16)	N3—H3X	0.8896
Mo1—C2 ⁱⁱ	2.1674 (16)	C3—C4	1.364 (2)
Mo1—C2 ⁱⁱⁱ	2.1674 (16)	C3—H3	0.9300
Mo1—C1 ⁱ	2.1690 (16)	C4—C5	1.398 (2)
Mo1—C1 ⁱⁱⁱ	2.1690 (16)	C4—H4	0.9300
Mo1—C1	2.1690 (16)	C5—C6	1.400 (2)
Mo1—C1 ⁱⁱ	2.1690 (16)	C5—C8	1.460 (2)
O1—H1A	0.8501	C6—C7	1.370 (2)
O1—H1B	0.8505	C6—H6	0.9300
N1—C1	1.157 (2)	C7—H7	0.9300
N2—C2	1.155 (2)	C8—C8 ⁱ	1.332 (3)
N3—C3	1.339 (2)	C8—H8	0.9300
C2—Mo1—C2 ⁱ	121.37 (8)	C1 ⁱⁱⁱ —Mo1—C1 ⁱⁱ	107.72 (8)
C2—Mo1—C2 ⁱⁱ	73.57 (8)	C1—Mo1—C1 ⁱⁱ	144.64 (8)
C2 ⁱ —Mo1—C2 ⁱⁱ	139.67 (8)	H1A—O1—H1B	105.6
C2—Mo1—C2 ⁱⁱⁱ	139.67 (8)	C3—N3—C7	121.66 (14)
C2 ⁱ —Mo1—C2 ⁱⁱⁱ	73.57 (8)	C3—N3—H3X	123.2
C2 ⁱⁱ —Mo1—C2 ⁱⁱⁱ	121.37 (8)	C7—N3—H3X	115.1
C2—Mo1—C1 ⁱ	72.33 (5)	N1—C1—Mo1	177.01 (13)
C2 ⁱ —Mo1—C1 ⁱ	74.09 (6)	N2—C2—Mo1	176.36 (14)
C2 ⁱⁱ —Mo1—C1 ⁱ	142.18 (5)	N3—C3—C4	120.35 (15)
C2 ⁱⁱⁱ —Mo1—C1 ⁱ	77.74 (6)	N3—C3—H3	119.8
C2—Mo1—C1 ⁱⁱⁱ	142.18 (5)	C4—C3—H3	119.8
C2 ⁱ —Mo1—C1 ⁱⁱⁱ	77.74 (6)	C3—C4—C5	120.08 (15)
C2 ⁱⁱ —Mo1—C1 ⁱⁱⁱ	72.33 (5)	C3—C4—H4	120.0
C2 ⁱⁱⁱ —Mo1—C1 ⁱⁱⁱ	74.09 (6)	C5—C4—H4	120.0
C1 ⁱ —Mo1—C1 ⁱⁱⁱ	144.64 (8)	C4—C5—C6	117.78 (14)
C2—Mo1—C1	74.09 (6)	C4—C5—C8	122.88 (14)
C2 ⁱ —Mo1—C1	72.33 (5)	C6—C5—C8	119.32 (14)
C2 ⁱⁱ —Mo1—C1	77.74 (6)	C7—C6—C5	119.78 (15)
C2 ⁱⁱⁱ —Mo1—C1	142.18 (5)	C7—C6—H6	120.1
C1 ⁱ —Mo1—C1	107.72 (8)	C5—C6—H6	120.1
C1 ⁱⁱⁱ —Mo1—C1	83.12 (8)	N3—C7—C6	120.27 (15)
C2—Mo1—C1 ⁱⁱ	77.74 (6)	N3—C7—H7	119.9
C2 ⁱ —Mo1—C1 ⁱⁱ	142.18 (5)	C6—C7—H7	119.9
C2 ⁱⁱ —Mo1—C1 ⁱⁱ	74.09 (6)	C8 ⁱ —C8—C5	124.74 (18)

C2 ⁱⁱⁱ —Mo1—C1 ⁱⁱ	72.33 (5)	C8 ⁱ —C8—H8	117.6
C1 ⁱ —Mo1—C1 ⁱⁱ	83.12 (8)	C5—C8—H8	117.6

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1A...N1 ^{iv}	0.85	2.11	2.9524 (19)	174
O1—H1B...N2 ^v	0.85	2.00	2.8195 (18)	162
N3—H3X...O1	0.89	1.86	2.7342 (17)	166

Symmetry codes: (iv) $x+1, y-1/2, -z$; (v) $-x+1/2, -y, z$.