

4,4'-Diazenediyl-dipyridinium (4-pyridyl-diazenyl)pyridinium octacyanidomolybdate(V) tetrahydrate

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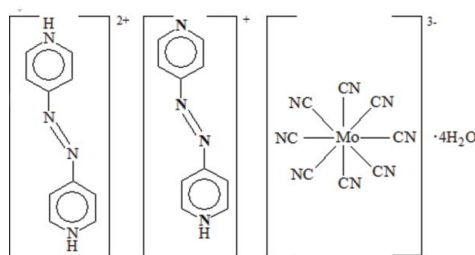
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 Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.033; wR factor = 0.065; data-to-parameter ratio = 15.3.

The structure of the title complex, $(\text{C}_{10}\text{H}_{10}\text{N}_4)(\text{C}_{10}\text{H}_9\text{N}_4)\text{[Mo(CN)}_8\text{]}\cdot 4\text{H}_2\text{O}$, consists of 4,4'-diazenediyl-dipyridinium and (4-pyridyldiazenyl)pyridinium cations disordered over the same site, an $[\text{Mo(CN)}_8]^{3-}$ anion and four uncoordinated water molecules. The cations (crystallographic symmetry, 2) and the $[\text{Mo(CN)}_8]^{3-}$ anion (crystallographic symmetry, 222) are arranged in an alternating fashion, forming a two-dimensional layered structure through hydrogen bonds. Hydrogen bonds, π - π stacking interactions (shortest distance = 4.7872 Å) and van der Waals forces between adjacent layers generate a three-dimensional supramolecular structure.

Related literature

For information on octacyanidometalate-based compounds complexes, see: Chelebaeva *et al.* (2008); Ikeda *et al.* (2005); Kosaka *et al.* (2007); Matoga *et al.* (2005); Prins *et al.* (2007); Przychodzeń *et al.* (2007); Wang *et al.* (2006).



Experimental

Crystal data

 $(\text{C}_{10}\text{H}_{10}\text{N}_4)(\text{C}_{10}\text{H}_9\text{N}_4)[\text{Mo(CN)}_8]\cdot 4\text{H}_2\text{O}$
 $M_r = 747.60$

 Orthorhombic, $Ccca$
 $a = 16.259$ (5) Å
 $b = 12.787$ (4) Å

 $c = 15.442$ (5) Å
 $V = 3210.5$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 0.47$ mm⁻¹
 $T = 291$ (2) K
 $0.28 \times 0.26 \times 0.24$ mm

Data collection

 Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2000)
 $T_{\text{min}} = 0.879$, $T_{\text{max}} = 0.895$

 13328 measured reflections
 1851 independent reflections
 1540 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.065$
 $S = 1.06$
 1851 reflections
 121 parameters

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.52$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3A}\cdots\text{O1}$	0.86 (4)	1.86 (4)	2.675 (3)	157 (3)
$\text{O1}-\text{H1A}\cdots\text{N2}^{\text{i}}$	0.85 (3)	2.06 (3)	2.809 (3)	147 (3)
$\text{O1}-\text{H1B}\cdots\text{N1}^{\text{ii}}$	0.85 (3)	2.40 (3)	3.164 (3)	150 (3)

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

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

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2078).

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supplementary materials

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4,4'-Diazenediylpyridinium (4-pyridyldiazenyl)pyridinium octacyanomolybdate(V) tetrahydrate

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Comment

Recently, the design and synthesis of multifunctional materials with lanthanide octacyanometalate-based metal assemblies are attracting much more interest (Chelebaeva *et al.*, 2008; Przychodzeń *et al.*, 2007; Ikeda *et al.*, 2005; Kosaka *et al.*, 2007; Matoga *et al.*, 2005; Wang *et al.*, 2006). The combination of the octacyanometalate $[M(\text{CN})_8]^{3-/4-}$ ($M = \text{Mo}, \text{W}$) building blocks with the lanthanide ions plays an important part in the construction of new supramolecular magnetic materials (Prins *et al.*, 2007). In search of a new lanthanide-containing octacyanometalate-based magnet using $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ and Ce^{3+} as the building blocks, we tried to employ 4,4'-azpy (4,4'-azobispyridine) as the primary ligand for coordination. However, the unexpected octacyanomolybdate(V)-based supramolecular complex $[\text{H}_3(4,4'\text{-azpy})_2][\text{Mo}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ without Ce^{3+} was obtained instead.

The title complex consists of $[\text{H}_2(4,4'\text{-azpy})]^{2+}$ and $[\text{H}(4,4'\text{-azpy})]^+$ cations disordered over the same site, $[\text{Mo}(\text{CN})_8]^{3-}$ anion and crystallized water molecules (Fig. 1). It is worth noting that $[\text{H}_2(4,4'\text{-azpy})]^{2+}$ and $[\text{H}(4,4'\text{-azpy})]^+$ cations are both disordered over the same site.

In the structure, the eight CN groups are all terminal ones and the average distance of Mo—C is 2.1582 Å. The center Mo atom is coordinated by eight cyano groups in a distorted square antiprism. $[\text{H}_2(4,4'\text{-azpy})]^{2+}$ cation, $[\text{H}(4,4'\text{-azpy})]^+$ cation (crystallographic symmetry, 2), and $[\text{Mo}(\text{CN})_8]^{3-}$ anion (crystallographic symmetry, 222) arranged in an alternating fashion to form a two-dimensional layered structure (Fig. 2) through O1—H1A \cdots N2 and N3—H3A \cdots O1 hydrogen-bonds. Then, a three-dimension supramolecular structure (Fig. 3) was formed through O1—H1B \cdots N1 hydrogen-bonds, π - π packing and Van der Waals forces between adjacent layers.

Experimental

Single crystals of the title complex were prepared at room temperature in the dark by slow diffusion of an acetonitrile solution (2 ml) containing both $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (21.71 mg, 0.05 mmol) and 4,4'-azpy (9.21 mg, 0.05 mmol) into an acetonitrile solution (20 ml) of $[\text{HN}(\text{n}-\text{C}_4\text{H}_9)_3]_3[\text{Mo}(\text{CN})_8] \cdot 4\text{H}_2\text{O}$ (46.60 mg, 0.05 mmol). After two weeks, pale yellow crystals were obtained.

Refinement

All non-H atoms were refined anisotropically. The (C,N)H atoms of the 4,4'-azpy molecules were placed in calculated positions with C—H and N—H distances 0.99 Å and 0.92 Å, respectively, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The H atoms of

supplementary materials

the solvent water molecules were located in a difference Fourier map and refined as riding, with O—H restraints of 0.95 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Figures

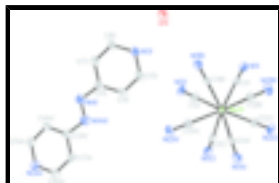


Fig. 1. Molecular structure of the title complex showing 30% probability displacement ellipsoids. H atoms are not shown for clarity.

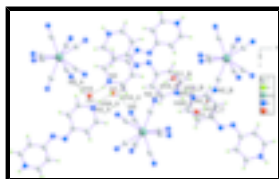


Fig. 2. View in the *ac* plane of the hydrogen-bonding interactions in the title complex. [Symmetry codes: A: 0.5 - *x*, 1.5 - *y*, 1 - *z*; B: 1/2 + *x*, *y*, 1 - *z*; C: 1 - *x*, 1.5 - *y*, *z*; D: 0.5 - *x*, -1/2 + *y*, 1.5 - *z*; E: 0.5 - *x*, 1 - *y*, *z*; F: *x*, 1.5 - *y*, 1.5 - *z*; G: 1 - *x*, 1 - *y*, 1 - *z*; H: 1/2 + *x*, 1.5 - *y*, -1/2 + *z*.]

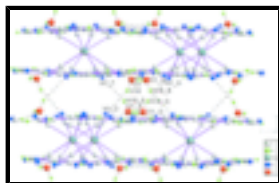


Fig. 3. The hydrogen-bonding interactions between adjacent layers in the title complex. [Symmetry codes: A: 0.5 - *x*, 1.5 - *y*, 1 - *z*; B: 1/2 + *x*, *y*, 1 - *z*; C: 1 - *x*, 1.5 - *y*, *z*; D: 0.5 - *x*, -1/2 + *y*, 1.5 - *z*; E: 0.5 - *x*, 1 - *y*, *z*; F: *x*, 1.5 - *y*, 1.5 - *z*; G: 1 - *x*, 1 - *y*, 1 - *z*; H: 1/2 + *x*, 1.5 - *y*, -1/2 + *z*.]

4,4'-Diazenediylidipyridinium (4-pyridyldiazenyl)pyridinium octacyanomolybdate(V) tetrahydrate

Crystal data

(C₁₀H₁₀N₄)(C₁₀H₉N₄)[Mo(CN)₈]·4H₂O

$M_r = 747.60$

Orthorhombic, *Ccca*

Hall symbol: -C 2b 2bc

$a = 16.259 (5) \text{ \AA}$

$b = 12.787 (4) \text{ \AA}$

$c = 15.442 (5) \text{ \AA}$

$V = 3210.5 (18) \text{ \AA}^3$

$Z = 4$

$F_{000} = 1524$

$D_x = 1.547 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 13328 reflections

$\theta = 2.4\text{--}27.5^\circ$

$\mu = 0.47 \text{ mm}^{-1}$

$T = 291 (2) \text{ K}$

Block, pale yellow

$0.28 \times 0.26 \times 0.24 \text{ mm}$

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291(2) \text{ K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2000)

1851 independent reflections

1540 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\text{max}} = 27.6^\circ$

$\theta_{\text{min}} = 2.4^\circ$

$h = -21 \rightarrow 21$

$T_{\min} = 0.879$, $T_{\max} = 0.895$
13328 measured reflections

$k = -16 \rightarrow 16$
 $l = -19 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2 + 2.9147P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1851 reflections	$(\Delta/\sigma)_{\max} < 0.001$
121 parameters	$\Delta\rho_{\max} = 0.52 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.39870 (13)	0.84531 (17)	0.79366 (15)	0.0382 (5)	
C2	0.45460 (14)	0.83539 (19)	0.63923 (15)	0.0427 (5)	
C3	0.41341 (15)	0.62509 (19)	0.31466 (17)	0.0461 (6)	
C4	0.43896 (15)	0.63527 (19)	0.40018 (17)	0.0447 (6)	
H4	0.4948	0.6385	0.4132	0.054*	
C5	0.38109 (14)	0.64066 (18)	0.46624 (17)	0.0450 (6)	
H5	0.3982	0.6474	0.5234	0.054*	
C6	0.27215 (16)	0.62570 (19)	0.36140 (16)	0.0464 (6)	
H6	0.2163	0.6225	0.3484	0.056*	
C7	0.33002 (14)	0.62029 (19)	0.29530 (16)	0.0441 (6)	
H7	0.3129	0.6135	0.2381	0.053*	
Mo1	0.5000	0.7500	0.7500	0.02552 (10)	
N1	0.34570 (12)	0.89415 (16)	0.81824 (14)	0.0468 (5)	
N2	0.43040 (13)	0.87856 (16)	0.57871 (13)	0.0462 (5)	
N3	0.29771 (12)	0.63591 (16)	0.44687 (13)	0.0437 (5)	

supplementary materials

H3A	0.262 (2)	0.639 (3)	0.488 (2)	0.052*	0.75
N4	0.46326 (12)	0.62255 (16)	0.24043 (15)	0.0495 (5)	
O1	0.17847 (11)	0.59099 (14)	0.56028 (11)	0.0457 (4)	
H1A	0.1323 (19)	0.593 (2)	0.535 (2)	0.069*	
H1B	0.1865 (18)	0.530 (2)	0.5803 (19)	0.069*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0371 (11)	0.0422 (12)	0.0353 (12)	0.0130 (9)	-0.0141 (9)	-0.0110 (9)
C2	0.0442 (13)	0.0452 (13)	0.0387 (13)	0.0103 (10)	-0.0093 (10)	0.0096 (10)
C3	0.0477 (13)	0.0468 (14)	0.0438 (14)	0.0125 (10)	0.0088 (11)	0.0055 (11)
C4	0.0376 (11)	0.0457 (13)	0.0510 (15)	0.0007 (9)	0.0096 (11)	0.0065 (11)
C5	0.0437 (13)	0.0476 (13)	0.0436 (14)	0.0068 (10)	0.0092 (11)	0.0120 (11)
C6	0.0499 (13)	0.0449 (13)	0.0443 (14)	0.0183 (10)	0.0102 (11)	-0.0136 (10)
C7	0.0453 (13)	0.0482 (14)	0.0388 (14)	0.0139 (10)	-0.0010 (11)	0.0019 (11)
Mo1	0.02788 (16)	0.02590 (16)	0.02278 (16)	0.000	0.000	0.000
N1	0.0505 (12)	0.0483 (11)	0.0417 (12)	0.0182 (9)	-0.0095 (9)	-0.0131 (9)
N2	0.0595 (13)	0.0422 (11)	0.0371 (11)	0.0099 (9)	-0.0119 (10)	0.0020 (9)
N3	0.0438 (11)	0.0452 (11)	0.0420 (12)	0.0206 (9)	0.0038 (9)	-0.0123 (9)
N4	0.0492 (10)	0.0498 (11)	0.0496 (13)	0.0047 (9)	0.0063 (11)	-0.0067 (10)
O1	0.0429 (9)	0.0484 (10)	0.0459 (11)	0.0129 (8)	0.0064 (8)	0.0155 (8)

Geometric parameters (\AA , $^\circ$)

C1—N1	1.130 (3)	C6—H6	0.9300
C1—Mo1	2.157 (2)	C7—H7	0.9300
C2—N2	1.155 (3)	Mo1—C1 ⁱ	2.157 (2)
C2—Mo1	2.159 (2)	Mo1—C1 ⁱⁱ	2.157 (2)
C3—C7	1.390 (3)	Mo1—C1 ⁱⁱⁱ	2.157 (2)
C3—C4	1.391 (4)	Mo1—C2 ⁱⁱⁱ	2.159 (2)
C3—N4	1.404 (3)	Mo1—C2 ⁱⁱ	2.159 (2)
C4—C5	1.389 (3)	Mo1—C2 ⁱ	2.159 (2)
C4—H4	0.9300	N3—H3A	0.86 (4)
C5—N3	1.390 (3)	N4—N4 ^{iv}	1.231 (4)
C5—H5	0.9300	O1—H1A	0.85 (3)
C6—N3	1.390 (3)	O1—H1B	0.85 (3)
C6—C7	1.390 (3)		
N1—C1—Mo1	178.5 (2)	C1 ⁱⁱ —Mo1—C2 ⁱⁱⁱ	77.12 (10)
N2—C2—Mo1	178.1 (2)	C1 ⁱⁱⁱ —Mo1—C2 ⁱⁱⁱ	72.59 (9)
C7—C3—C4	120.0 (2)	C1 ⁱ —Mo1—C2	77.12 (10)
C7—C3—N4	112.7 (2)	C1—Mo1—C2	72.59 (9)
C4—C3—N4	127.2 (2)	C1 ⁱⁱ —Mo1—C2	74.20 (9)
C5—C4—C3	120.0 (2)	C1 ⁱⁱⁱ —Mo1—C2	142.59 (9)
C5—C4—H4	120.0	C2 ⁱⁱⁱ —Mo1—C2	75.23 (13)
C3—C4—H4	120.0	C1 ⁱ —Mo1—C2 ⁱⁱ	142.59 (9)

C4—C5—N3	120.0 (2)	C1—Mo1—C2 ⁱⁱ	74.20 (9)
C4—C5—H5	120.0	C1 ⁱⁱ —Mo1—C2 ⁱⁱ	72.59 (9)
N3—C5—H5	120.0	C1 ⁱⁱⁱ —Mo1—C2 ⁱⁱ	77.12 (10)
N3—C6—C7	120.0 (2)	C2 ⁱⁱⁱ —Mo1—C2 ⁱⁱ	140.02 (13)
N3—C6—H6	120.0	C2—Mo1—C2 ⁱⁱ	119.25 (14)
C7—C6—H6	120.0	C1 ⁱ —Mo1—C2 ⁱ	72.59 (9)
C3—C7—C6	120.0 (2)	C1—Mo1—C2 ⁱ	77.12 (10)
C3—C7—H7	120.0	C1 ⁱⁱ —Mo1—C2 ⁱ	142.59 (9)
C6—C7—H7	120.0	C1 ⁱⁱⁱ —Mo1—C2 ⁱ	74.20 (9)
C1 ⁱ —Mo1—C1	80.44 (12)	C2 ⁱⁱⁱ —Mo1—C2 ⁱ	119.25 (14)
C1 ⁱ —Mo1—C1 ⁱⁱ	143.57 (12)	C2—Mo1—C2 ⁱ	140.02 (13)
C1—Mo1—C1 ⁱⁱ	111.19 (13)	C2 ⁱⁱ —Mo1—C2 ⁱ	75.23 (13)
C1 ⁱ —Mo1—C1 ⁱⁱⁱ	111.19 (13)	C5—N3—C6	120.0 (2)
C1—Mo1—C1 ⁱⁱⁱ	143.57 (12)	C5—N3—H3A	120 (2)
C1 ⁱⁱ —Mo1—C1 ⁱⁱⁱ	80.44 (12)	C6—N3—H3A	120 (2)
C1 ⁱ —Mo1—C2 ⁱⁱⁱ	74.20 (9)	N4 ^{iv} —N4—C3	111.4 (3)
C1—Mo1—C2 ⁱⁱⁱ	142.59 (9)	H1A—O1—H1B	109 (3)

Symmetry codes: (i) $x, -y+3/2, -z+3/2$; (ii) $-x+1, y, -z+3/2$; (iii) $-x+1, -y+3/2, z$; (iv) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3A \cdots O1	0.86 (4)	1.86 (4)	2.675 (3)	157 (3)
O1—H1A \cdots N2 ^v	0.85 (3)	2.06 (3)	2.809 (3)	147 (3)
O1—H1B \cdots N1 ^{vi}	0.85 (3)	2.40 (3)	3.164 (3)	150 (3)

Symmetry codes: (v) $-x+1/2, -y+3/2, -z+1$; (vi) $-x+1/2, y-1/2, -z+3/2$.

Fig. 1

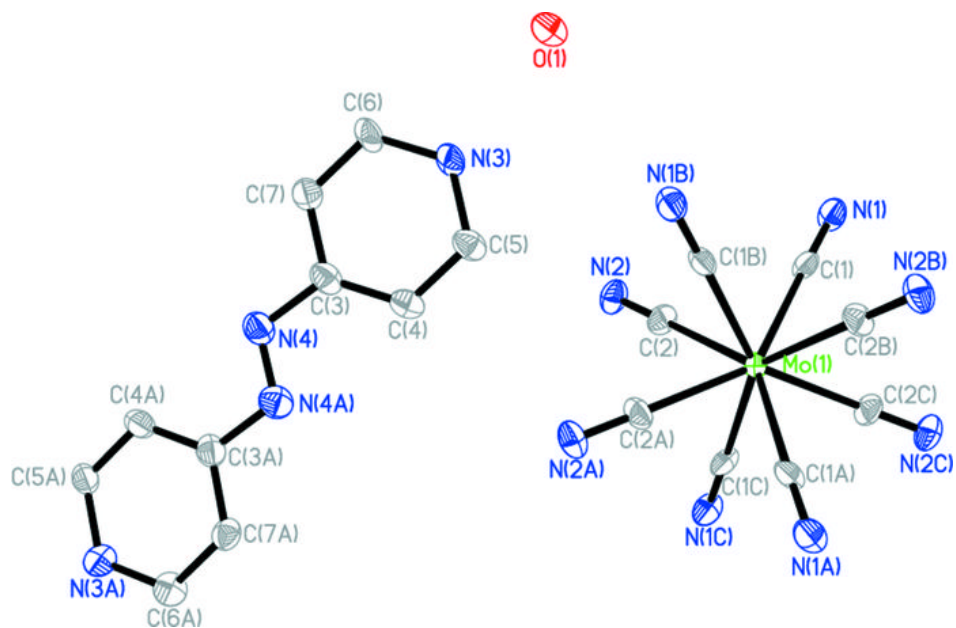


Fig. 2

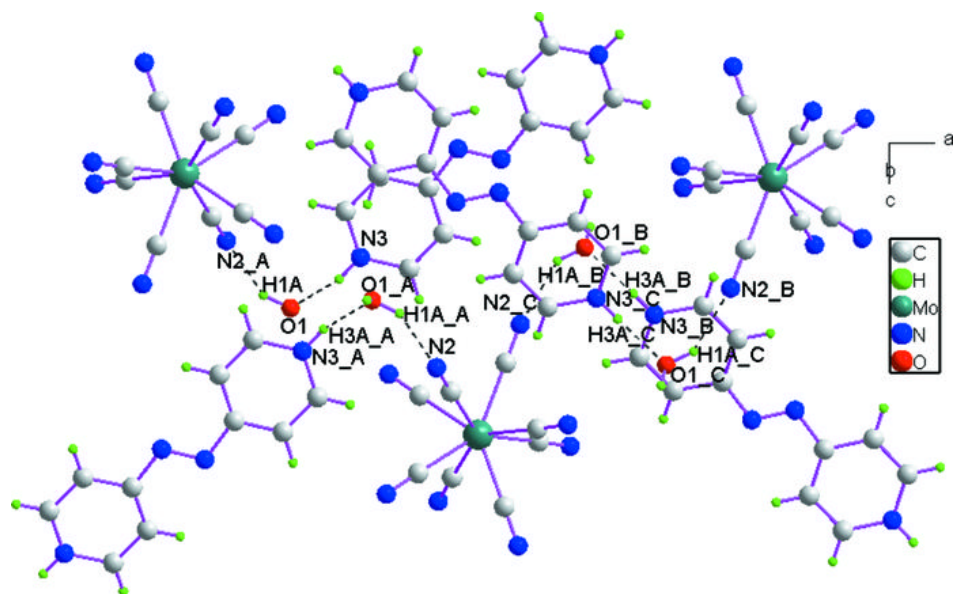


Fig. 3

