

2,6-Diaminopyridinium bis(4-hydroxypyridine-2,6-dicarboxylato- $\kappa^3 O^2, N, O^6$)-chromate(III) dihydrate

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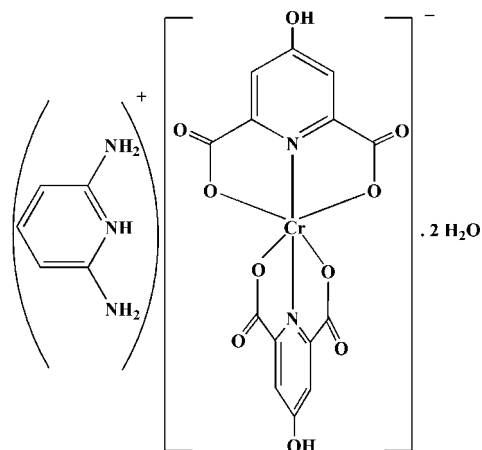
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.042; wR factor = 0.105; data-to-parameter ratio = 15.6.

The reaction of chromium(III) nitrate hexahydrate, pyridine-2,6-diamine and 4-hydroxypyridine-2,6-dicarboxylic acid in a 1:2:2 molar ratio in aqueous solution resulted in the formation of the title compound, $(C_5H_8N_3)[Cr(C_7H_3NO_5)_2] \cdot 2H_2O$ or $(pydaH)[Cr(hypydc)_2] \cdot 2H_2O$ (where $pyda$ is pyridine-2,6-diamine and $hypydcH_2$ is 4-hydroxypyridine-2,6-dicarboxylic acid). Each Cr^{III} atom is hexacoordinated by four O and two N atoms from two $(hypydc)^{2-}$ fragments, which act as tridentate ligands, in a distorted octahedral geometry. The $O-Cr-O-C$ torsion angles between the two planes of the $(hypydc)^{2-}$ fragments [$-99.81(17)$ and $97.77(17)^\circ$] indicate that these two units are almost perpendicular to one another. In the crystal structure, extensive $O-H \cdots O$, $N-H \cdots O$ and $C-H \cdots O$ hydrogen bonds with $D \cdots A$ distances ranging from 2.560 (2) to 3.279 (3) Å, ion pairing, $C-O \cdots \pi$ [$O \cdots \pi = 3.166(2)$ Å] and $\pi-\pi$ stacking interactions between $(hypydc)^{2-}$ and $(pydaH)^+$ rings [with a centroid-centroid distance of 3.3353 (14) Å] contribute to the formation of a three-dimensional supramolecular structure.

Related literature

For related literature, see: Aghabozorg *et al.*, (2007); Aghabozorg, Manteghi *et al.* (2008); Aghabozorg, Saadaty *et al.* (2008); Ranjbar *et al.* (2001); Soleimannejad *et al.* (2008).



Experimental

Crystal data

$(C_5H_8N_3)[Cr(C_7H_3NO_5)_2] \cdot 2H_2O$
 $M_r = 560.38$
 Monoclinic, $P2_1/n$
 $a = 6.9590(4)$ Å
 $b = 20.9904(12)$ Å
 $c = 14.8951(8)$ Å
 $\beta = 95.3030(13)^\circ$

$V = 2166.4(2)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.61$ mm⁻¹
 $T = 100(2)$ K
 $0.32 \times 0.08 \times 0.07$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{min} = 0.829$, $T_{max} = 0.959$

24511 measured reflections
 5229 independent reflections
 3694 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.078$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.104$
 $S = 1.02$
 5229 reflections

336 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.47$ e Å⁻³
 $\Delta\rho_{min} = -0.57$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3NA \cdots O2^i$	0.87	2.03	2.840 (3)	154
$N4-H4NB \cdots O11^i$	0.87	2.09	2.958 (3)	173
$N4-H4NA \cdots O3^{ii}$	0.87	2.33	3.122 (3)	151
$N5-H5NB \cdots O8$	0.87	1.99	2.831 (3)	162
$N5-H5NA \cdots O2^i$	0.87	2.01	2.812 (3)	152
$O5-H5O \cdots O12$	0.80	1.77	2.560 (2)	169
$O10-H10O \cdots O11^{iii}$	0.80	1.83	2.624 (3)	173
$O11-H11C \cdots O1$	0.82	1.92	2.719 (2)	163
$O11-H11D \cdots O7^{iv}$	0.82	1.90	2.709 (3)	169
$O12-H12A \cdots O9^v$	0.82	2.01	2.809 (3)	165
$O12-H12B \cdots O4^{ii}$	0.82	2.05	2.872 (3)	177
$C16-H16A \cdots O3^{ii}$	0.95	2.49	3.265 (3)	139
$C18-H18A \cdots O12^{vi}$	0.95	2.59	3.279 (3)	130

Symmetry codes: (i) $-x, -y+2, -z$; (ii) $x-\frac{1}{2}, -y+\frac{5}{2}, z-\frac{1}{2}$; (iii) $-x+1, -y+2, -z+1$; (iv) $x-1, y, z$; (v) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{3}{2}$; (vi) $x-\frac{1}{2}, -y+\frac{5}{2}, z+\frac{1}{2}$

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YM2072).

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supplementary materials

Acta Cryst. (2008). E64, m1208-m1209 [doi:10.1107/S1600536808027347]

2,6-Diaminopyridinium bis(4-hydroxypyridine-2,6-dicarboxylato- κ^3O^2,N,O^6)chromate(III) dihydrate

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Comment

The molecular structure of the title compound is shown in Fig. 1. Hydrogen bond geometries are given in Table 1. According to the crystal structure, the title compound is composed of an anionic complex, $[\text{Cr}(\text{hypydc})_2]^-$, protonated diamino-2,6-pyridinium as a counter ion, $(\text{pydaH})^+$, and two uncoordinated water molecules. This compound crystallizes in the monoclinic system, space group $P2_1/n$ with four molecules in the unit cell.

The Cr^{III} atom is six-coordinated by two 4-hydroxypyridine-2,6-dicarboxylate, $(\text{hypydc})^{2-}$, groups which act as tridentate ligand through one pyridine N atom and two carboxylate O atoms. N1 and N2 atoms of two $(\text{hypydc})^{2-}$ fragments occupy the axial position, while O1, O3, O6 and O8 atoms form the equatorial plane. The N1—Cr1—N2 angle [$177.33(9)^\circ$] deviates slightly from linearity. Therefore, the coordination geometry around Cr^{III} can be described as distorted octahedral. The bond angles O6—Cr1—O1, O3—Cr1—O6, O3—Cr1—O8 and O1—Cr1—O8 ($93.28(7)^\circ$, $93.82(7)^\circ$, $90.88(7)^\circ$ and $91.46(7)^\circ$, respectively), and the O1—Cr1—O6—C13 and O8—Cr1—O1—C6 torsion angles ($-99.81(17)^\circ$ and $97.77(17)^\circ$, respectively) show that these two $(\text{hypydc})^{2-}$ groups are almost perpendicular. Furthermore, the bond angles O1—Cr1—O3 [$156.06(7)^\circ$] and O6—Cr1—O8 [$156.99(7)^\circ$] indicate that four carboxylate groups of the two dianions are in a flattened tetrahedral arrangement around the Cr^{III} atom.

In the crystal structure of $(\text{pydaH})[\text{Cr}(\text{hypydc})_2] \cdot 2\text{H}_2\text{O}$, the spaces between to layers of $[\text{Cr}(\text{hypydc})_2]^-$ anions are filled with $(\text{pydaH})^+$ cations and water molecules. There are also π - π stacking interactions between the aromatic ring of the coordinated $(\text{hypydc})^{2-}$ anion and the aromatic ring of the $(\text{pydaH})^+$ cation with distances of 3.3353 (14) Å for $Cg1 \cdots Cg2$. There are also $\text{C}-\text{O} \cdots \pi$ stacking interactions between C6—O2 and $Cg1$ with $\text{O} \cdots \pi$ distance of 3.166 (2) Å ($1-x, 2-y, -z$) [$Cg1$ and $Cg2$ are the centroid for (N1/C1—C5) and (N3/C15—C19) rings, respectively] (Fig. 2).

Intermolecular $\text{O}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonding with $\text{D} \cdots \text{A}$ ranging from 2.560 (2) to 3.279 (3) Å, ionpairing, π - π and $\text{C}-\text{O} \cdots \pi$ stacking interactions seem to be effective in the stabilization of the crystal structure, resulting in the formation of an interesting supramolecular structure (Fig. 3).

Experimental

An aqueous solution of CrCl_3 (24 mg, 0.15 mmol), pyridine-2,6-diamine (32 mg, 0.3 mmol) and 4-Hydroxypyridine-2,6-dicarboxylic acid (54 mg, 0.3 mmol) was added to each other in a 1:2:2 molar ratio, and the reaction mixture was heated at about 50°C for 4 h. Violet crystals of the title compound were obtained from the solution after two weeks at room temperature.

Refinement

The hydrogen atoms of NH₂ and OH groups and also H atoms of water molecule were found in difference Fourier synthesis. The hydrogen atoms of the H(C) atom positions were calculated. All Hydrogen atoms were refined in isotropic approximation in riding model with the $U_{\text{iso}}(\text{H})$ parameters equal to 1.2 $U_{\text{eq}}(\text{Xi})$, where $U(\text{Xi})$ the equivalent thermal parameters of the carbon or nitrogen or oxygen atom to which corresponding H atom is bonded.

Figures

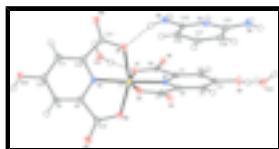


Fig. 1. Molecular structure of (pydaH)[Cr(hypydc)₂].2H₂O, hydrogen bonds are shown as dashed lines and thermal ellipsoids are at 50% probability level.

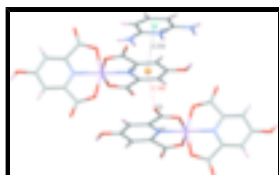


Fig. 2. The π - π and C—O \cdots π stacking interactions with the distances.

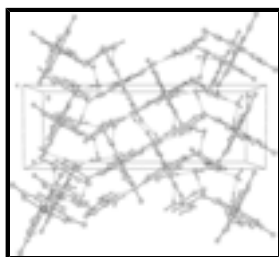


Fig. 3. Crystal packing of the title compound showing the three dimensional H-bonded framework.

2,6-Diaminopyridinium bis(4-hydroxypyridine-2,6-dicarboxylato- $\kappa^3\text{O}^2,\text{N},\text{O}^6$)chromate(III) dihydrate

Crystal data

(C₅H₈N₃)[Cr(C₇H₃N₁O₅)₂].2H₂O

$M_r = 560.38$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 6.9590$ (4) Å

$b = 20.9904$ (12) Å

$c = 14.8951$ (8) Å

$\beta = 95.3030$ (13)°

$V = 2166.4$ (2) Å³

$Z = 4$

$F_{000} = 1148$

$D_x = 1.718$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1320 reflections

$\theta = 3$ – 28°

$\mu = 0.61$ mm⁻¹

$T = 100$ (2) K

Needle, black

$0.32 \times 0.08 \times 0.07$ mm

Data collection

Bruker APEXII CCD area-detector' diffractometer	5229 independent reflections
Radiation source: fine-focus sealed tube	3694 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.078$
$T = 100(2)$ K	$\theta_{\text{max}} = 28.0^\circ$
ω scans	$\theta_{\text{min}} = 1.7^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.829$, $T_{\text{max}} = 0.959$	$k = -27 \rightarrow 27$
24511 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.042$	H-atom parameters constrained
$wR(F^2) = 0.104$	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.9675P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
5229 reflections	$(\Delta/\sigma)_{\text{max}} = 0.002$
336 parameters	$\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.57 \text{ e } \text{\AA}^{-3}$
	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	$U_{\text{iso}}^*/U_{\text{eq}}$
Cr1	0.46263 (6)	1.098248 (19)	0.20578 (3)	0.00992 (10)
O1	0.3226 (2)	1.01686 (8)	0.17083 (11)	0.0124 (4)
O2	0.1871 (3)	0.95887 (8)	0.05618 (11)	0.0141 (4)
O3	0.5836 (2)	1.18207 (8)	0.18501 (11)	0.0127 (4)
O4	0.6584 (3)	1.25241 (8)	0.08081 (12)	0.0154 (4)
O5	0.3766 (3)	1.11140 (8)	-0.20081 (11)	0.0166 (4)

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H5O	0.4037	1.1423	-0.2284	0.020*
O6	0.7149 (2)	1.05418 (8)	0.23449 (11)	0.0138 (4)
O7	0.9177 (3)	1.01550 (9)	0.34882 (12)	0.0192 (4)
O8	0.2157 (2)	1.14101 (8)	0.23077 (11)	0.0135 (4)
O9	0.0389 (3)	1.17639 (9)	0.33928 (12)	0.0174 (4)
O10	0.5003 (3)	1.09070 (9)	0.61131 (11)	0.0190 (4)
H10O	0.6029	1.0846	0.6388	0.023*
O11	0.1788 (3)	0.93417 (8)	0.28815 (12)	0.0159 (4)
H11D	0.0901	0.9544	0.3071	0.019*
H11C	0.2300	0.9525	0.2480	0.046 (11)*
O12	0.4442 (3)	1.21870 (8)	-0.27326 (12)	0.0170 (4)
H12A	0.4497	1.2508	-0.2418	0.020*
H12B	0.3656	1.2273	-0.3160	0.020*
N1	0.4410 (3)	1.10250 (10)	0.07265 (13)	0.0106 (4)
N2	0.4719 (3)	1.09238 (9)	0.33828 (13)	0.0105 (4)
N3	-0.0320 (3)	1.16527 (10)	-0.07279 (13)	0.0117 (4)
H3NA	-0.0906	1.1294	-0.0859	0.014*
N4	-0.0433 (3)	1.19284 (11)	-0.22368 (14)	0.0178 (5)
H4NB	-0.0924	1.1563	-0.2413	0.021*
H4NA	-0.0025	1.2175	-0.2648	0.032 (9)*
N5	-0.0454 (3)	1.13054 (10)	0.07407 (14)	0.0135 (4)
H5NB	0.0119	1.1350	0.1281	0.016*
H5NA	-0.0986	1.0961	0.0506	0.016*
C1	0.3476 (3)	1.05598 (11)	0.02427 (16)	0.0101 (5)
C2	0.3233 (4)	1.05809 (12)	-0.06822 (16)	0.0117 (5)
H2A	0.2573	1.0250	-0.1019	0.014*
C3	0.3993 (3)	1.11092 (11)	-0.11176 (16)	0.0108 (5)
C4	0.4932 (3)	1.15980 (12)	-0.05965 (16)	0.0110 (5)
H4A	0.5443	1.1959	-0.0876	0.013*
C5	0.5088 (3)	1.15376 (11)	0.03232 (16)	0.0108 (5)
C6	0.2781 (3)	1.00555 (11)	0.08605 (16)	0.0105 (5)
C7	0.5931 (3)	1.20100 (12)	0.10225 (16)	0.0111 (5)
C8	0.6272 (4)	1.06604 (12)	0.38294 (16)	0.0123 (5)
C9	0.6455 (4)	1.06333 (12)	0.47589 (16)	0.0122 (5)
H9A	0.7555	1.0444	0.5078	0.015*
C10	0.4959 (4)	1.08960 (11)	0.52222 (16)	0.0137 (5)
C11	0.3335 (4)	1.11654 (12)	0.47336 (17)	0.0137 (5)
H11A	0.2305	1.1339	0.5032	0.016*
C12	0.3287 (4)	1.11698 (11)	0.38087 (16)	0.0117 (5)
C13	0.7689 (4)	1.04231 (12)	0.31917 (16)	0.0128 (5)
C14	0.1782 (4)	1.14746 (11)	0.31450 (16)	0.0118 (5)
C15	0.0192 (4)	1.20629 (12)	-0.13776 (17)	0.0132 (5)
C16	0.1308 (4)	1.25899 (12)	-0.11129 (17)	0.0149 (5)
H16A	0.1713	1.2879	-0.1549	0.018*
C17	0.1819 (4)	1.26871 (12)	-0.02048 (17)	0.0138 (5)
H17A	0.2600	1.3044	-0.0023	0.017*
C18	0.1230 (4)	1.22815 (12)	0.04490 (17)	0.0135 (5)
H18A	0.1551	1.2368	0.1071	0.016*
C19	0.0162 (4)	1.17463 (12)	0.01759 (16)	0.0122 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.0125 (2)	0.0104 (2)	0.00680 (19)	0.00029 (16)	0.00056 (14)	-0.00067 (15)
O1	0.0170 (9)	0.0115 (9)	0.0083 (9)	-0.0017 (7)	0.0000 (7)	0.0004 (6)
O2	0.0167 (9)	0.0123 (9)	0.0131 (9)	-0.0027 (7)	0.0006 (7)	-0.0010 (7)
O3	0.0161 (9)	0.0135 (9)	0.0084 (9)	-0.0023 (7)	0.0003 (7)	-0.0013 (7)
O4	0.0189 (10)	0.0120 (9)	0.0149 (10)	-0.0027 (8)	-0.0011 (7)	0.0010 (7)
O5	0.0284 (11)	0.0143 (10)	0.0068 (9)	-0.0023 (8)	0.0011 (7)	0.0021 (7)
O6	0.0143 (9)	0.0156 (9)	0.0114 (9)	0.0019 (7)	0.0014 (7)	-0.0015 (7)
O7	0.0170 (10)	0.0241 (11)	0.0161 (10)	0.0082 (8)	-0.0007 (7)	-0.0006 (8)
O8	0.0135 (9)	0.0175 (9)	0.0092 (9)	0.0023 (7)	-0.0002 (7)	-0.0007 (7)
O9	0.0177 (10)	0.0214 (10)	0.0134 (10)	0.0071 (8)	0.0029 (7)	-0.0001 (7)
O10	0.0214 (10)	0.0279 (11)	0.0073 (9)	0.0029 (8)	-0.0010 (7)	-0.0002 (7)
O11	0.0169 (10)	0.0181 (10)	0.0136 (9)	0.0020 (8)	0.0052 (7)	0.0022 (7)
O12	0.0230 (10)	0.0145 (9)	0.0128 (9)	-0.0013 (8)	-0.0018 (7)	0.0020 (7)
N1	0.0102 (10)	0.0101 (10)	0.0117 (10)	0.0019 (8)	0.0014 (8)	-0.0019 (8)
N2	0.0125 (10)	0.0100 (10)	0.0088 (10)	0.0002 (8)	0.0003 (8)	-0.0009 (8)
N3	0.0133 (11)	0.0102 (10)	0.0118 (11)	-0.0008 (8)	0.0018 (8)	0.0010 (8)
N4	0.0215 (12)	0.0190 (12)	0.0125 (11)	-0.0055 (10)	-0.0010 (9)	0.0041 (9)
N5	0.0147 (11)	0.0158 (11)	0.0097 (10)	-0.0018 (9)	-0.0007 (8)	-0.0002 (8)
C1	0.0092 (12)	0.0094 (12)	0.0118 (12)	0.0024 (9)	0.0024 (9)	-0.0006 (9)
C2	0.0116 (12)	0.0098 (12)	0.0132 (13)	0.0025 (9)	-0.0008 (9)	-0.0012 (9)
C3	0.0117 (12)	0.0140 (13)	0.0066 (11)	0.0042 (10)	0.0001 (9)	-0.0002 (9)
C4	0.0102 (12)	0.0115 (12)	0.0114 (12)	0.0030 (9)	0.0018 (9)	0.0018 (9)
C5	0.0081 (12)	0.0110 (12)	0.0134 (13)	0.0015 (9)	0.0017 (9)	-0.0007 (9)
C6	0.0103 (12)	0.0116 (12)	0.0099 (12)	0.0025 (10)	0.0030 (9)	0.0002 (9)
C7	0.0088 (12)	0.0133 (12)	0.0113 (12)	0.0031 (10)	0.0011 (9)	-0.0018 (9)
C8	0.0129 (13)	0.0105 (12)	0.0134 (13)	-0.0018 (10)	-0.0002 (10)	-0.0004 (9)
C9	0.0140 (13)	0.0112 (12)	0.0110 (12)	0.0022 (10)	-0.0014 (9)	0.0005 (9)
C10	0.0201 (13)	0.0110 (12)	0.0098 (12)	-0.0014 (10)	0.0008 (10)	0.0015 (9)
C11	0.0160 (13)	0.0123 (12)	0.0132 (13)	-0.0016 (10)	0.0037 (10)	-0.0013 (9)
C12	0.0122 (12)	0.0100 (12)	0.0124 (12)	-0.0020 (9)	-0.0011 (9)	-0.0021 (9)
C13	0.0154 (13)	0.0117 (12)	0.0113 (12)	-0.0009 (10)	0.0011 (10)	-0.0017 (9)
C14	0.0145 (13)	0.0109 (12)	0.0098 (12)	-0.0008 (10)	0.0005 (9)	0.0003 (9)
C15	0.0130 (13)	0.0143 (13)	0.0123 (13)	0.0050 (10)	0.0016 (10)	0.0030 (9)
C16	0.0150 (13)	0.0125 (13)	0.0173 (14)	0.0019 (10)	0.0030 (10)	0.0039 (10)
C17	0.0111 (12)	0.0088 (12)	0.0214 (14)	0.0015 (10)	0.0010 (10)	-0.0017 (10)
C18	0.0120 (13)	0.0130 (13)	0.0154 (13)	0.0014 (10)	0.0000 (10)	-0.0025 (10)
C19	0.0090 (12)	0.0152 (13)	0.0123 (13)	0.0034 (10)	-0.0001 (9)	-0.0002 (9)

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

Cr1—N2	1.973 (2)	N4—C15	1.343 (3)
Cr1—N1	1.977 (2)	N4—H4NB	0.8700
Cr1—O3	1.9872 (17)	N4—H4NA	0.8700
Cr1—O6	1.9957 (18)	N5—C19	1.347 (3)
Cr1—O8	2.0036 (17)	N5—H5NB	0.8700

supplementary materials

Cr1—O1	2.0111 (17)	N5—H5NA	0.8701
O1—C6	1.294 (3)	C1—C2	1.373 (3)
O2—C6	1.227 (3)	C1—C6	1.511 (3)
O3—C7	1.303 (3)	C2—C3	1.412 (3)
O4—C7	1.225 (3)	C2—H2A	0.9500
O5—C3	1.321 (3)	C3—C4	1.410 (3)
O5—H5O	0.7999	C4—C5	1.370 (3)
O6—C13	1.306 (3)	C4—H4A	0.9500
O7—C13	1.225 (3)	C5—C7	1.516 (3)
O8—C14	1.305 (3)	C8—C9	1.380 (3)
O9—C14	1.229 (3)	C8—C13	1.515 (3)
O10—C10	1.325 (3)	C9—C10	1.413 (3)
O10—H10O	0.8000	C9—H9A	0.9500
O11—H11D	0.8199	C10—C11	1.405 (4)
O11—H11C	0.8201	C11—C12	1.375 (3)
O12—H12A	0.8198	C11—H11A	0.9500
O12—H12B	0.8201	C12—C14	1.514 (3)
N1—C5	1.339 (3)	C15—C16	1.388 (4)
N1—C1	1.345 (3)	C16—C17	1.382 (4)
N2—C12	1.334 (3)	C16—H16A	0.9500
N2—C8	1.335 (3)	C17—C18	1.384 (4)
N3—C15	1.367 (3)	C17—H17A	0.9500
N3—C19	1.371 (3)	C18—C19	1.387 (3)
N3—H3NA	0.8701	C18—H18A	0.9500
N2—Cr1—N1	177.33 (9)	C5—C4—H4A	120.9
N2—Cr1—O3	103.64 (8)	C3—C4—H4A	120.9
N1—Cr1—O3	78.35 (8)	N1—C5—C4	121.6 (2)
N2—Cr1—O6	79.04 (8)	N1—C5—C7	110.3 (2)
N1—Cr1—O6	102.70 (8)	C4—C5—C7	128.0 (2)
O3—Cr1—O6	93.82 (7)	O2—C6—O1	124.7 (2)
N2—Cr1—O8	77.96 (8)	O2—C6—C1	121.4 (2)
N1—Cr1—O8	100.31 (8)	O1—C6—C1	113.9 (2)
O3—Cr1—O8	90.88 (7)	O4—C7—O3	124.6 (2)
O6—Cr1—O8	156.99 (7)	O4—C7—C5	121.8 (2)
N2—Cr1—O1	100.15 (8)	O3—C7—C5	113.6 (2)
N1—Cr1—O1	77.79 (8)	N2—C8—C9	120.8 (2)
O3—Cr1—O1	156.06 (7)	N2—C8—C13	111.6 (2)
O6—Cr1—O1	93.28 (7)	C9—C8—C13	127.6 (2)
O8—Cr1—O1	91.46 (7)	C8—C9—C10	118.0 (2)
C6—O1—Cr1	118.37 (15)	C8—C9—H9A	121.0
C7—O3—Cr1	118.46 (15)	C10—C9—H9A	121.0
C3—O5—H5O	120.7	O10—C10—C11	117.1 (2)
C13—O6—Cr1	117.65 (15)	O10—C10—C9	123.1 (2)
C14—O8—Cr1	118.36 (15)	C11—C10—C9	119.8 (2)
C10—O10—H10O	116.5	C12—C11—C10	117.7 (2)
H11D—O11—H11C	113.6	C12—C11—H11A	121.1
H12A—O12—H12B	104.7	C10—C11—H11A	121.1
C5—N1—C1	121.1 (2)	N2—C12—C11	121.6 (2)
C5—N1—Cr1	119.27 (16)	N2—C12—C14	110.8 (2)

C1—N1—Cr1	119.54 (16)	C11—C12—C14	127.5 (2)
C12—N2—C8	121.9 (2)	O7—C13—O6	126.4 (2)
C12—N2—Cr1	119.67 (17)	O7—C13—C8	120.2 (2)
C8—N2—Cr1	118.33 (16)	O6—C13—C8	113.4 (2)
C15—N3—C19	123.3 (2)	O9—C14—O8	124.9 (2)
C15—N3—H3NA	122.3	O9—C14—C12	122.0 (2)
C19—N3—H3NA	114.3	O8—C14—C12	113.1 (2)
C15—N4—H4NB	123.8	N4—C15—N3	117.4 (2)
C15—N4—H4NA	116.6	N4—C15—C16	124.2 (2)
H4NB—N4—H4NA	117.1	N3—C15—C16	118.5 (2)
C19—N5—H5NB	111.0	C17—C16—C15	118.9 (2)
C19—N5—H5NA	117.8	C17—C16—H16A	120.6
H5NB—N5—H5NA	127.1	C15—C16—H16A	120.6
N1—C1—C2	121.5 (2)	C16—C17—C18	122.1 (2)
N1—C1—C6	110.4 (2)	C16—C17—H17A	118.9
C2—C1—C6	128.1 (2)	C18—C17—H17A	118.9
C1—C2—C3	118.0 (2)	C17—C18—C19	118.5 (2)
C1—C2—H2A	121.0	C17—C18—H18A	120.7
C3—C2—H2A	121.0	C19—C18—H18A	120.7
O5—C3—C4	123.6 (2)	N5—C19—N3	116.8 (2)
O5—C3—C2	116.9 (2)	N5—C19—C18	124.5 (2)
C4—C3—C2	119.5 (2)	N3—C19—C18	118.7 (2)
C5—C4—C3	118.2 (2)		
N2—Cr1—O1—C6	175.80 (17)	C3—C4—C5—C7	-176.5 (2)
N1—Cr1—O1—C6	-2.46 (16)	Cr1—O1—C6—O2	-177.36 (19)
O3—Cr1—O1—C6	2.3 (3)	Cr1—O1—C6—C1	2.3 (3)
O6—Cr1—O1—C6	-104.75 (17)	N1—C1—C6—O2	179.2 (2)
O8—Cr1—O1—C6	97.77 (17)	C2—C1—C6—O2	-0.1 (4)
N2—Cr1—O3—C7	-177.73 (16)	N1—C1—C6—O1	-0.5 (3)
N1—Cr1—O3—C7	0.44 (17)	C2—C1—C6—O1	-179.8 (2)
O6—Cr1—O3—C7	102.64 (17)	Cr1—O3—C7—O4	177.52 (19)
O8—Cr1—O3—C7	-99.91 (17)	Cr1—O3—C7—C5	-0.6 (3)
O1—Cr1—O3—C7	-4.3 (3)	N1—C5—C7—O4	-177.7 (2)
N2—Cr1—O6—C13	-0.10 (17)	C4—C5—C7—O4	0.4 (4)
N1—Cr1—O6—C13	-178.02 (17)	N1—C5—C7—O3	0.5 (3)
O3—Cr1—O6—C13	103.07 (17)	C4—C5—C7—O3	178.6 (2)
O8—Cr1—O6—C13	1.7 (3)	C12—N2—C8—C9	-0.1 (4)
O1—Cr1—O6—C13	-99.81 (17)	Cr1—N2—C8—C9	176.98 (18)
N2—Cr1—O8—C14	2.31 (17)	C12—N2—C8—C13	-179.5 (2)
N1—Cr1—O8—C14	-179.77 (17)	Cr1—N2—C8—C13	-2.4 (3)
O3—Cr1—O8—C14	-101.46 (17)	N2—C8—C9—C10	-0.4 (4)
O6—Cr1—O8—C14	0.5 (3)	C13—C8—C9—C10	178.9 (2)
O1—Cr1—O8—C14	102.37 (17)	C8—C9—C10—O10	-178.7 (2)
O3—Cr1—N1—C5	-0.11 (17)	C8—C9—C10—C11	0.9 (4)
O6—Cr1—N1—C5	-91.45 (18)	O10—C10—C11—C12	178.6 (2)
O8—Cr1—N1—C5	88.65 (18)	C9—C10—C11—C12	-1.0 (4)
O1—Cr1—N1—C5	177.91 (19)	C8—N2—C12—C11	0.0 (4)
O3—Cr1—N1—C1	-175.84 (19)	Cr1—N2—C12—C11	-176.99 (18)
O6—Cr1—N1—C1	92.83 (18)	C8—N2—C12—C14	176.2 (2)

supplementary materials

O8—Cr1—N1—C1	-87.08 (18)	Cr1—N2—C12—C14	-0.8 (3)
O1—Cr1—N1—C1	2.18 (17)	C10—C11—C12—N2	0.5 (4)
O3—Cr1—N2—C12	87.31 (19)	C10—C11—C12—C14	-175.0 (2)
O6—Cr1—N2—C12	178.62 (19)	Cr1—O6—C13—O7	179.5 (2)
O8—Cr1—N2—C12	-0.64 (18)	Cr1—O6—C13—C8	-1.1 (3)
O1—Cr1—N2—C12	-89.97 (19)	N2—C8—C13—O7	-178.4 (2)
O3—Cr1—N2—C8	-89.81 (18)	C9—C8—C13—O7	2.3 (4)
O6—Cr1—N2—C8	1.50 (18)	N2—C8—C13—O6	2.2 (3)
O8—Cr1—N2—C8	-177.77 (19)	C9—C8—C13—O6	-177.1 (2)
O1—Cr1—N2—C8	92.91 (18)	Cr1—O8—C14—O9	174.9 (2)
C5—N1—C1—C2	2.1 (3)	Cr1—O8—C14—C12	-3.3 (3)
Cr1—N1—C1—C2	177.73 (18)	N2—C12—C14—O9	-175.7 (2)
C5—N1—C1—C6	-177.3 (2)	C11—C12—C14—O9	0.2 (4)
Cr1—N1—C1—C6	-1.6 (3)	N2—C12—C14—O8	2.6 (3)
N1—C1—C2—C3	-0.1 (3)	C11—C12—C14—O8	178.5 (2)
C6—C1—C2—C3	179.1 (2)	C19—N3—C15—N4	-177.6 (2)
C1—C2—C3—O5	179.0 (2)	C19—N3—C15—C16	2.1 (4)
C1—C2—C3—C4	-1.2 (3)	N4—C15—C16—C17	178.2 (2)
O5—C3—C4—C5	-179.6 (2)	N3—C15—C16—C17	-1.5 (4)
C2—C3—C4—C5	0.6 (3)	C15—C16—C17—C18	-1.0 (4)
C1—N1—C5—C4	-2.7 (3)	C16—C17—C18—C19	2.8 (4)
Cr1—N1—C5—C4	-178.40 (18)	C15—N3—C19—N5	179.4 (2)
C1—N1—C5—C7	175.5 (2)	C15—N3—C19—C18	-0.3 (4)
Cr1—N1—C5—C7	-0.2 (3)	C17—C18—C19—N5	178.2 (2)
C3—C4—C5—N1	1.4 (4)	C17—C18—C19—N3	-2.1 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3NA \cdots O2 ⁱ	0.87	2.03	2.840 (3)	154
N4—H4NB \cdots O11 ⁱ	0.87	2.09	2.958 (3)	173
N4—H4NA \cdots O3 ⁱⁱ	0.87	2.33	3.122 (3)	151
N5—H5NB \cdots O8	0.87	1.99	2.831 (3)	162
N5—H5NA \cdots O2 ⁱ	0.87	2.01	2.812 (3)	152
O5—H5O \cdots O12	0.80	1.77	2.560 (2)	169
O10—H10O \cdots O11 ⁱⁱⁱ	0.80	1.83	2.624 (3)	173
O11—H11C \cdots O1	0.82	1.92	2.719 (2)	163
O11—H11D \cdots O7 ^{iv}	0.82	1.90	2.709 (3)	169
O12—H12A \cdots O9 ^v	0.82	2.01	2.809 (3)	165
O12—H12B \cdots O4 ⁱⁱ	0.82	2.05	2.872 (3)	177
C16—H16A \cdots O3 ⁱⁱ	0.95	2.49	3.265 (3)	139
C18—H18A \cdots O12 ^{vi}	0.95	2.59	3.279 (3)	130

Symmetry codes: (i) $-x, -y+2, -z$; (ii) $x-1/2, -y+5/2, z-1/2$; (iii) $-x+1, -y+2, -z+1$; (iv) $x-1, y, z$; (v) $x+1/2, -y+5/2, z-1/2$; (vi) $x-1/2, -y+5/2, z+1/2$.

Fig. 1

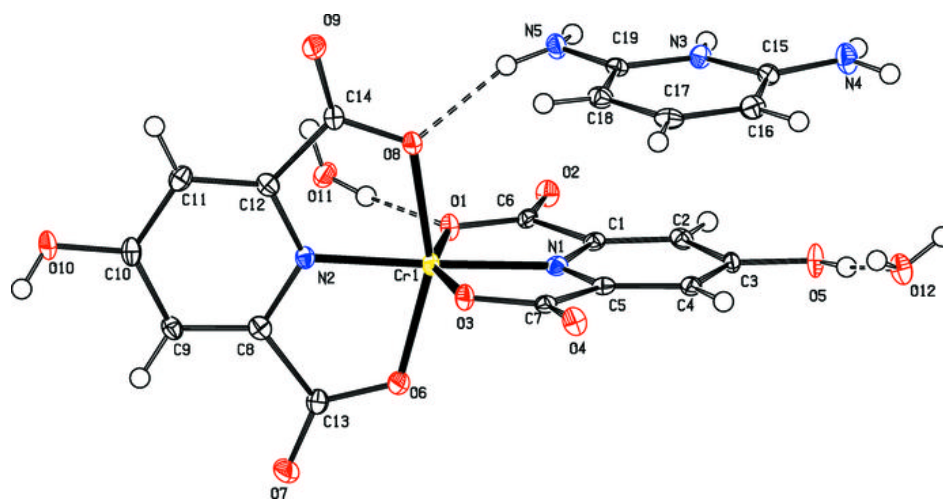


Fig. 2

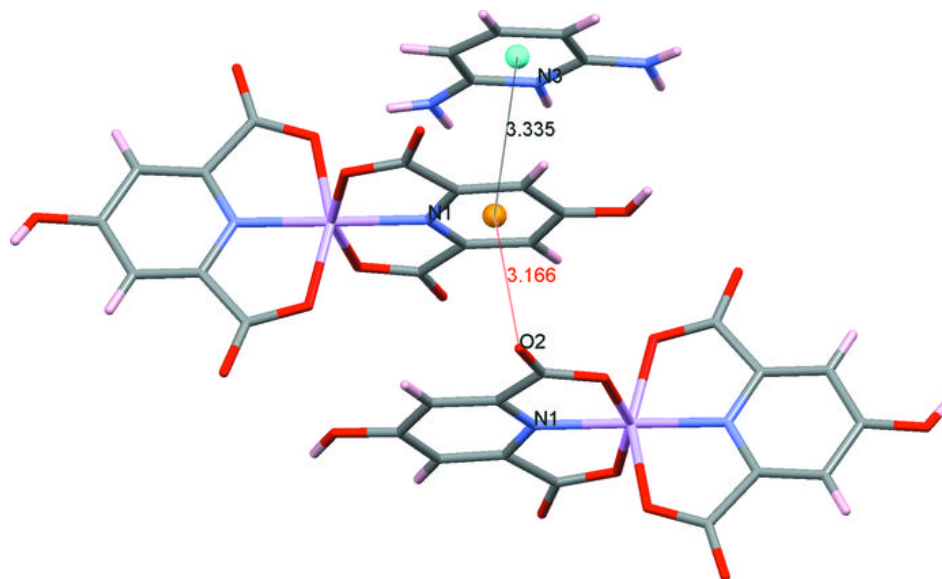


Fig. 3

