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Crystal structure of ammonium bis(pyridine-2,6-dicarboxylato-κ^3O,N,O')chromate(III) from synchrotron data

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The structure of the title compound, $(NH_4)[Cr(pydc)_2]$ (pydc is pyridine-2,6-dicarboxylate, $C_7H_3NO_4$), has been determined from synchrotron data. The Cr^{III} ion and the N atom of the ammonium cation are located on a crystallographic fourfold rotoinversion axis ($\bar{4}$). The Cr^{III} cation is coordinated by four O atoms and the two N atoms of two meridional pydc ligands, displaying a distorted octahedral geometry. The Cr—N and Cr—O bond lengths are 1.9727 (15) and 1.9889 (9) Å, respectively. The crystal structure is stabilized by intermolecular hydrogen bonds involving the N–H groups of the ammonium cation and pyridine C–H groups as donors and the non-coordinating carbonyl O atoms as acceptors.

1. Chemical context

Pyridine-2,6-dicarboxylic acid (also known as dipicolinic acid and abbreviated here as H_2pydc) can coordinate a metal center as a neutral molecule (H_2pydc), the univalent anion ($Hpydc^-$), or the divalent anion ($pydc^{2-}$). In particular, the pyridine-2,6-dicarboxylate ligand frequently acts as a meridional tridentate ligand and sometimes also as a bidentate or bridging ligand (Park *et al.*, 2007). The first $[Cr(pydc)_2]^-$ complex was prepared as the Na^+ salt according to the literature (Hoggard & Schmidtke, 1973) and its crystal structure determined using synchrotron data. Structural analysis showed the compound to be a dihydrate (Dai *et al.*, 2006; González-Baró *et al.*, 2008) rather than the 1.5 or 2.5 hydrates that had been suggested previously (Hoggard & Schmidtke, 1973; Fürst *et al.*, 1979). The crystal structures of $K[Cr(pydc)_2]$ (Hakimi *et al.*, 2012) and $Rb[Cr(pydc)_2]$ (Fürst *et al.*, 1979) have also been reported previously but the structure of the ammonium salt is not known.

OPEN ACCESS
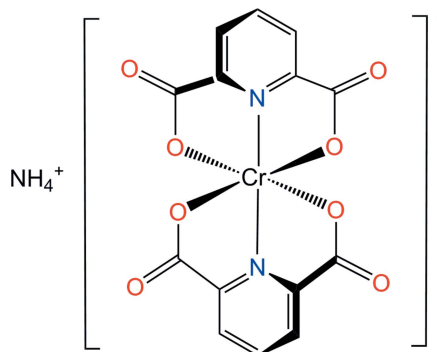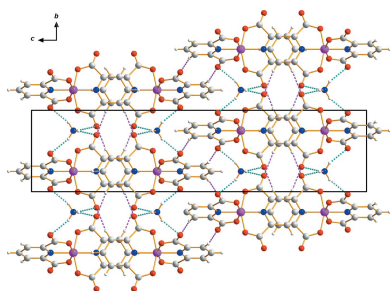
Here we report the crystal structure of $(NH_4)[Cr(pydc)_2]$ in order to clarify unambiguously the bonding mode of the two

Figure 1
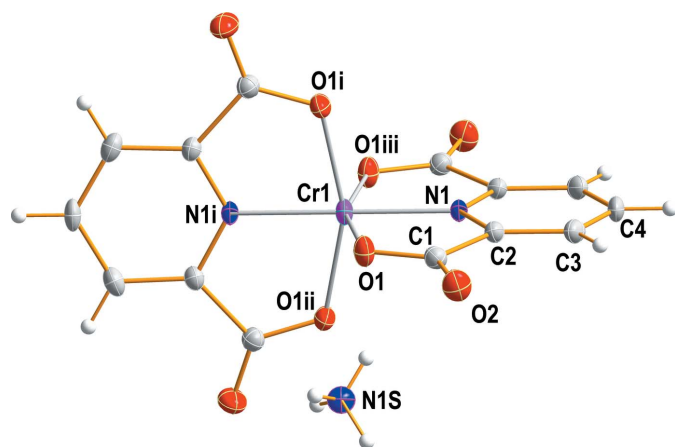The molecular structure of (NH$_4$)[Cr(pydc)$_2$], showing the atom-numbering scheme. Non-H atoms are shown as displacement ellipsoids drawn at the 50% probability level.

pyridine-2,6-dicarboxylato ligands and the structural arrangement of this ammonium salt.

2. Structural commentary

Counter-ionic species play a very important role in coordination chemistry. The structure reported here is another example of a [Cr(pydc)$_2$]$^-$ salt but with a different cation. The structural analysis shows that the two tridentate pyridine-2,6-dicarboxylate (pydc) dianions octahedrally coordinate to the Cr^{III} metal center through one N atom and two carboxylate O atoms in a meridional arrangement. The Cr^{III} ion is located on a crystallographic fourfold rotoinversion axis ($\bar{4}$). An ellipsoid plot of title complex together with the atomic numbering is illustrated in Fig. 1.

The Cr—N and Cr—O bond lengths to the pydc^{2-} ligands are 1.9727 (15) and 1.9889 (9) Å, respectively, and these lengths agree well with the values observed in the literature for complexes with the same [Cr(pydc)$_2$]$^-$ anion (Fürst *et al.*, 1979; Dai *et al.*, 2006; González-Baró *et al.*, 2008; Zhou *et al.*, 2009; Hakimi *et al.*, 2012). The coordinating pyridine N atoms are in a mutually *trans* arrangement. Both tridentate pydc^{2-} ligands are nearly planar and are oriented perpendicular to one another. Bond angles about the central chromium atom are 79.10 (3) for N1—Cr1—O1, 100.90 (3) for N1—Cr1—O1^i and 158.20 (5)° for O1^i—Cr1—O1^{ii}, indicating a distorted octahedral coordination environment [symmetry codes: (i) $-y + \frac{5}{4}, x - \frac{3}{4}, -z + \frac{5}{4}$; (ii) $y + \frac{3}{4}, -x + \frac{5}{4}, -z + \frac{5}{4}$]. The C1—O1 and C1—O2 bond lengths within the carboxylate group of the pydc^{2-} ligand are 1.2941 (15) and 1.2223 (14) Å, respectively, and can be compared with values of 1.298 (5) and 1.224 (5) Å for Rb[Cr(pydc)$_2$] (Fürst *et al.*, 1979). The ammonium cation, also lying on a crystallographic fourfold rotoinversion axis ($\bar{4}$), shows a distorted tetrahedral geometry of the hydrogen atoms around the central nitrogen atom with N—H distances of 0.846 (9) Å and the H—N—H angles ranging from 105.36 (9) to 118.06 (9)°.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$O2^i	0.93	2.50	3.4071 (15)	167
N1S—H1$S\cdots$O2^{ii}	0.85 (1)	2.04 (1)	2.8462 (11)	158 (2)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{3}{2}, -z + \frac{3}{2}$; (ii) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{5}{4}$.

3. Supramolecular features

The pattern of hydrogen bonding around the cation is very similar to the coordination environment in the related potassium salt (Hakimi *et al.*, 2012). The non-coordinating carbonyl O atom forms weak C—H$\cdots$O hydrogen bonds that contribute to the crystal packing. The ammonium cation is also linked to the carbonyl O atoms from four neighboring pydc^{2-} ligands through classical N—H$\cdots$O hydrogen bonds (Table 1). An extensive array of these contacts generate a three-dimensional network of molecules stacked along the *a*-axis direction (Fig. 2). π–π interactions involving adjacent pyridine rings further link the components of the structure into a three-dimensional network. The centroid–centroid distance between the π–π stacked rings (N1/C2–C4/C3^{iv}/C2^{iv})$\cdots$(N1^v/C2^v–C4^v/C3^{vi}/C2^{vi}) is 3.572 (2) Å [symmetry codes: (iv) $2 - x, \frac{1}{2} - y, z$; (v) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (vi) $\frac{5}{2} - x, \frac{1}{2} - y, \frac{3}{2} - z$].

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, May 2014 with one update; Groom & Allen, 2014) indicates a total of 16 hits for Cr^{III} complexes with a complex anion [Cr(pydc)$_2$]$^-$ unit. Many crystal structures of [Cr(pydc)$_2$]$^-$ with inorganic, organic or complex counter-cations such as K$^+$ (Hakimi *et al.*, 2012), Na$^+$ (Dai *et al.*, 2006; González-Baró *et al.*, 2008; Zhou *et al.*, 2009), Rb$^+$ (Fürst *et al.*, 1979), creatH$^+$ (creat = creatinine; Aghabozorg *et al.*, 2008), 4,4'-bpyH$^+$ (bpy
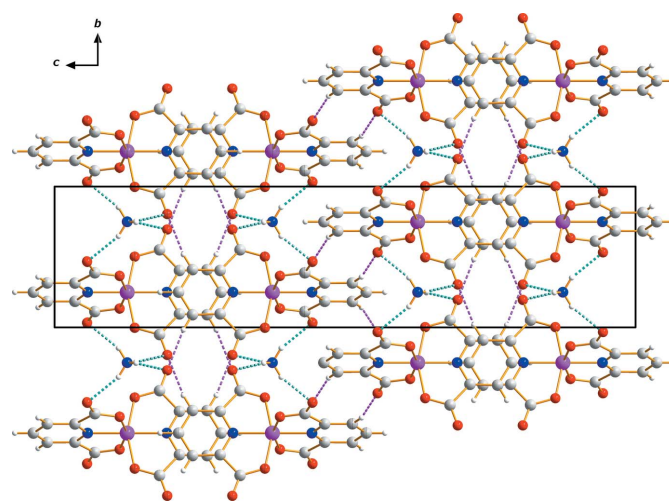

Figure 2
Crystal packing of (NH$_4$)[Cr(pydc)$_2$], viewed perpendicular to the *bc* plane. Dashed lines represent C—H$\cdots$O (purple) and N—H$\cdots$O (blue) hydrogen-bonding interactions.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(NH_4)[Cr(C_7H_3NO_4)_2]$
M_r	400.25
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature (K)	301
a, c (Å)	7.0305 (10), 28.995 (6)
V (Å³)	1433.2 (5)
Z	4
Radiation type	Synchrotron, $\lambda = 0.62998$ Å
μ (mm⁻¹)	0.62
Crystal size (mm)	$0.15 \times 0.10 \times 0.10$
Data collection	
Diffractometer	ADSC Q210 CCD area detector
Absorption correction	Empirical (using intensity measurements) (*HKL3000sm SCALEPACK*; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.925, 0.940
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6841, 943, 903
R_{int}	0.052
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.695
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.081, 1.21
No. of reflections	943
No. of parameters	63
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.31, −0.86

Computer programs: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2008, 2015b), *DIAMOND* (Brandenburg, 2007) and *publCIF* (Westrip 2010).

= bipyridine; Soleimannejad *et al.*, 2008), dmpH⁺ (dmp = 2,9-dimethyl-1,10-phenanthrone; Aghajani *et al.*, 2009), 2-apymH⁺ (2-apym = 2-aminopyrimidine; Eshtiagh-Hosseini *et al.*, 2010), [Cr(tpy)(pydc)]⁺ [tpy = 2,6-bis(2-pyridyl)pyridine; Casellato *et al.*, 1991] and [Ag(atr)₂]⁺ (atr = 3-amino-1*H*-1,2,4-triazole; Tabatabaee *et al.*, 2011) have been determined.

Alternative coordination behaviors of the pydc ligands are found in [Cu(Hpydc)₂]·3H₂O, which has one neutral H₂pydc and one divalent pydc²⁻ ligand, while [Ni(Hpydc)₂]·3H₂O (Nathan & Mai, 2000) has two meridional univalent Hpydc⁻ ligands. The ligands in [Ni(cyclam)(Hpydc)₂]·2H₂O (Park *et al.*, 2007) and Na₂[Pt(Hpydc)₂]·6H₂O are monodentate and bidentate, respectively, while Hpydc⁻ is tridentate in the complexes [Cu(Hpydc)₂]·3H₂O and [Ni(Hpydc)₂]·3H₂O (Nathan & Mai, 2000).

5. Synthesis and crystallization

All chemicals were reagent-grade materials and were used without further purification. The starting material, Na[Cr(pydc)₂]·2H₂O was prepared as described previously (Hoggard & Schmidtke, 1973). The sodium salt (0.20 g) was dissolved in 15 mL of water at 323 K and added to 3 mL of water containing 0.5 g of NH₄Cl. The resulting solution was filtered and allowed to stand at room temperature for several days to give brown block-like crystals of the ammonium salt NH₄[Cr(pydc)₂] suitable for X-ray structural analysis.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (ring H atoms) and with $U_{iso}(H) = 1.2\, U_{eq}$(parent atom). The H atoms of the ammonium cation were located from difference Fourier maps and refined with restraints and a fixed N—H distance of 0.87 Å, with $U_{iso}(H) = 1.2U_{eq}(N)$. One reflection with $F_o <<< F_c$ was omitted from the final refinement cycles. The slightly low fraction of measured reflections results from the geometry of the 2D-SMC beamline goniostat.

References

Aghabozorg, H., Derikvand, Z., Olmstead, M. M. & Attar Gharamaleki, J. (2008). *Acta Cryst.* E**64**, m1234–m1235.
Aghajani, Z., Aghabozorg, H., Sadr-Khanlou, E., Shokrollahi, A., Derki, S. & Shamsipur, M. (2009). *J. Iran. Chem. Soc.* **6**, 373–385.
Arvai, A. J. & Nielsen, C. (1983). *ADSC Quantum-210 ADX*. Area Detector System Corporation, Poway, CA, USA.
Brandenburg, K. (2007). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Casellato, U., Graziani, R., Bonomo, R. P. & Di Bilio, A. J. (1991). *J. Chem. Soc. Dalton Trans.* pp. 23–31.
Dai, Y., Shi, W., Zhu, X.-J., Zhao, B. & Cheng, P. (2006). *Inorg. Chim. Acta*, **359**, 3353–3358.
Eshtiagh-Hosseini, H., Yousefi, Z., Mirzaei, M., Chen, Y.-G., Beyramabadi, S. A., Shokrollahi, A. & Aghaei, R. (2010). *J. Mol. Struct.* **973**, 1–8.
Fürst, W., Gouzerh, P. & Jeannin, Y. (1979). *J. Coord. Chem.* **8**, 237–243.
González-Baró, A. C., Pis-Diez, R., Piro, O. E. & Parajón-Costa, B. S. (2008). *Polyhedron*, **27**, 502–512.
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
Hakimi, M., Kukovec, B.-M. & Minoura, M. (2012). *J. Chem. Crystallogr.* **42**, 290–294.
Hoggard, P. E. & Schmidtke, H.-H. (1973). *Inorg. Chem.* **12**, 1986–1990.
Nathan, L. C. & Mai, T. D. (2000). *J. Chem. Crystallogr.* **30**, 509–518.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. Academic Press, New York.
Park, H., Lough, A. J., Kim, J. C., Jeong, M. H. & Kang, Y. S. (2007). *Inorg. Chim. Acta*, **360**, 2819–2823.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015a). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015b). *Acta Cryst.* C**71**, 3–8.
Soleimannejad, J., Aghabozorg, H. & Hooshmand, S. (2008). *Acta Cryst.* E**64**, m564–m565.
Tabatabaee, M., Kukovec, B.-M. & Kazeroonizadeh, M. (2011). *Polyhedron*, **30**, 1114–1119.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zhou, Y., Yue, L. & Liu, J. (2009). *Inorg. Chem. Commun.* **12**, 1085–1087.

Crystal structure of ammonium bis(pyridine-2,6-dicarboxylato-$\kappa^3O,N,O′$)chromate(III) from synchrotron data

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Computing details

Data collection: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2008, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *publCIF* (Westrip 2010).

Bis(pyridine-2,6-dicarboxylato-$\kappa^3O,N,O′$)chromate(III)

Crystal data

(NH$_4$)[Cr(C$_7$H$_3$NO$_4$)$_2$]	$D_x = 1.855$ Mg m^{-3}
$M_r = 400.25$	Synchrotron radiation, $\lambda = 0.62998$ Å
Tetragonal, $I4_1/a$	Cell parameters from 20017 reflections
$a = 7.0305$ (10) Å	$\theta = 0.4–33.6°$
$c = 28.995$ (6) Å	$\mu = 0.62$ mm^{-1}
$V = 1433.2$ (5) Å^3	$T = 301$ K
$Z = 4$	Block, brown
$F(000) = 812$	$0.15 \times 0.10 \times 0.10$ mm

Data collection

ADSC Q210 CCD area detector diffractometer	6841 measured reflections
	943 independent reflections
Radiation source: PLSII 2D bending magnet	903 reflections with $I > 2\sigma(I)$
ω scan	$R_{int} = 0.052$
Absorption correction: empirical (using intensity measurements) (*HKL3000sm SCALEPACK*; Otwinowski & Minor, 1997)	$\theta_{max} = 26.0°$, $\theta_{min} = 4.0°$
	$h = -9 \rightarrow 9$
	$k = -9 \rightarrow 9$
	$l = -36 \rightarrow 36$
$T_{min} = 0.925$, $T_{max} = 0.940$	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.028$	
$wR(F^2) = 0.081$	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.7347P]$
$S = 1.21$	where $P = (F_o^2 + 2F_c^2)/3$
943 reflections	$(\Delta/\sigma)_{max} = 0.001$
63 parameters	$\Delta\rho_{max} = 0.31$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.86$ 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 ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
Cr1	1.0000	0.2500	0.6250	0.01282 (14)
O1	0.88412 (13)	0.50247 (12)	0.63797 (3)	0.0205 (2)
O2	0.78279 (14)	0.69538 (13)	0.69398 (4)	0.0261 (2)
N1	1.0000	0.2500	0.69303 (5)	0.0133 (3)
C1	0.86229 (15)	0.55077 (15)	0.68071 (4)	0.0163 (2)
C2	0.93527 (14)	0.40403 (15)	0.71495 (4)	0.0142 (2)
C3	0.93425 (15)	0.41005 (17)	0.76260 (4)	0.0189 (2)
H3	0.8912	0.5171	0.7783	0.023*
C4	1.0000	0.2500	0.78645 (6)	0.0201 (3)
H4	1.0000	0.2500	0.8185	0.024*
N1S	0.5000	0.7500	0.6250	0.0223 (4)
H1S	0.502 (3)	0.8529 (19)	0.6099 (7)	0.027*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.01591 (16)	0.01591 (16)	0.0066 (2)	0.000	0.000	0.000
O1	0.0286 (4)	0.0193 (4)	0.0134 (5)	0.0055 (3)	−0.0013 (3)	0.0013 (3)
O2	0.0304 (5)	0.0222 (4)	0.0258 (5)	0.0098 (3)	−0.0009 (3)	−0.0037 (3)
N1	0.0146 (5)	0.0171 (6)	0.0082 (7)	0.0008 (4)	0.000	0.000
C1	0.0159 (4)	0.0170 (5)	0.0160 (6)	0.0004 (3)	−0.0013 (4)	−0.0005 (4)
C2	0.0133 (4)	0.0175 (4)	0.0117 (5)	0.0001 (3)	−0.0005 (3)	−0.0016 (3)
C3	0.0171 (5)	0.0258 (5)	0.0137 (6)	−0.0006 (4)	0.0005 (3)	−0.0059 (4)
C4	0.0199 (7)	0.0324 (8)	0.0078 (8)	−0.0021 (5)	0.000	0.000
N1S	0.0220 (6)	0.0220 (6)	0.0229 (12)	0.000	0.000	0.000

Geometric parameters (Å, º)

Cr1—N1	1.9727 (15)	N1—C2	1.3355 (12)
Cr1—N1[i]	1.9727 (15)	C1—C2	1.5208 (15)
Cr1—O1	1.9889 (9)	C2—C3	1.3824 (16)
Cr1—O1[ii]	1.9889 (9)	C3—C4	1.3993 (15)
Cr1—O1[i]	1.9889 (9)	C3—H3	0.9300
Cr1—O1[iii]	1.9889 (9)	C4—C3[iii]	1.3992 (15)
O1—C1	1.2941 (15)	C4—H4	0.9300
O2—C1	1.2223 (14)	N1S—H1S	0.846 (9)
N1—C2[iii]	1.3354 (12)		
N1—Cr1—N1[i]	180.0	C2[iii]—N1—C2	123.19 (15)

N1—Cr1—O1	79.10 (3)	C2^{iii}—N1—Cr1	118.40 (7)
N1^i—Cr1—O1	100.90 (3)	C2—N1—Cr1	118.41 (7)
N1—Cr1—O1^{ii}	100.90 (3)	O2—C1—O1	125.02 (11)
N1^i—Cr1—O1^{ii}	79.10 (3)	O2—C1—C2	120.87 (11)
O1—Cr1—O1^{ii}	92.049 (10)	O1—C1—C2	114.02 (9)
N1—Cr1—O1^i	100.90 (3)	N1—C2—C3	120.14 (11)
N1^i—Cr1—O1^i	79.10 (3)	N1—C2—C1	110.77 (10)
O1—Cr1—O1^i	92.049 (10)	C3—C2—C1	129.04 (10)
O1^{ii}—Cr1—O1^i	158.20 (5)	C2—C3—C4	117.88 (11)
N1—Cr1—O1^{iii}	79.10 (3)	C2—C3—H3	121.1
N1^i—Cr1—O1^{iii}	100.90 (3)	C4—C3—H3	121.1
O1—Cr1—O1^{iii}	158.20 (5)	C3^{iii}—C4—C3	120.77 (16)
O1^{ii}—Cr1—O1^{iii}	92.049 (10)	C3^{iii}—C4—H4	119.6
O1^i—Cr1—O1^{iii}	92.049 (10)	C3—C4—H4	119.6
C1—O1—Cr1	117.64 (7)		
Cr1—O1—C1—O2	−175.18 (9)	O1—C1—C2—N1	−2.76 (12)
Cr1—O1—C1—C2	1.39 (12)	O2—C1—C2—C3	−3.27 (17)
C2^{iii}—N1—C2—C3	0.47 (7)	O1—C1—C2—C3	−179.99 (10)
Cr1—N1—C2—C3	−179.53 (7)	N1—C2—C3—C4	−0.90 (14)
C2^{iii}—N1—C2—C1	−177.04 (9)	C1—C2—C3—C4	176.10 (9)
Cr1—N1—C2—C1	2.96 (9)	C2—C3—C4—C3^{iii}	0.44 (7)
O2—C1—C2—N1	173.96 (9)		

Symmetry codes: (i) $y+3/4$, $−x+5/4$, $−z+5/4$; (ii) $−y+5/4$, $x−3/4$, $−z+5/4$; (iii) $−x+2$, $−y+1/2$, z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O2^{iv}	0.93	2.50	3.4071 (15)	167
N1S—H1S···O2^v	0.85 (1)	2.04 (1)	2.8462 (11)	158 (2)

Symmetry codes: (iv) $−x+3/2$, $−y+3/2$, $−z+3/2$; (v) $−y+5/4$, $x+1/4$, $−z+5/4$.