metal-organic compounds

Bis(4-carboxypyridinium) aquapentakis-(isothiocyanato-κN)iron(III) bis(pyridinium-4-carboxylate)

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In the crystal structure of the title compound, $(C_6H_6NO_2)_2$-$[Fe(NCS)_5(H_2O)]\cdot 2C_6H_5NO_2$, the iron complex lies on a mirror plane; the six-coordinate Fe^{III} ion, the coordinated water molecule and three of the five isothiocyanate ligands are located on this plane. The crystal structure is triple-layered. The pyridinium-4-carboxylate (ina) molecules and the protonated 4-carboxypyridinium (inaH$^+$) cations interact with each other through N—H···O and O—H···O hydrogen bonds, leading to the formation of a layer perpendicular to the b axis. Pairs of these layers sandwich another layer of $\{[Fe(NCS)_5\text{-}(H_2O)]^{2-}\}_n$ anions with which they interact via electrostatic attraction and O—H···O hydrogen bonds, resulting in sheets of triple layers also perpendicular to the b axis.

Related literature

For related compounds, see Li, Tong et al. (2004); Li, Zhao et al. (2004); Li et al. (2007).
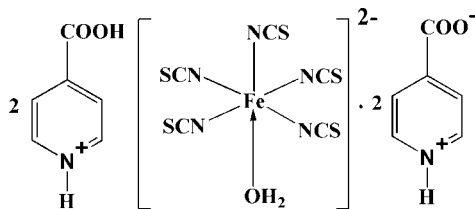
Experimental

Crystal data

$(C_6H_6NO_2)_2[Fe(NCS)_5(H_2O)]\cdot$ $2C_6H_5NO_2$
M_r = 858.72
Orthorhombic, $Pnma$
a = 14.8713 (3) Å
b = 21.0882 (3) Å
c = 11.9741 (2) Å
V = 3755.18 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.74 mm^{-1}
T = 297 (2) K
$0.36 \times 0.30 \times 0.20$ mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.776, T_{max} = 0.866
18247 measured reflections
3405 independent reflections
2589 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.132
S = 1.05
3405 reflections
265 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O11	0.76 (4)	1.95 (4)	2.711 (3)	178 (5)
N11—H11A···O11^i	0.86 (4)	1.86 (4)	2.710 (3)	168 (4)
O21—H21···O12^i	0.82	1.72	2.532 (3)	173
N21—H21A···O22^{ii}	0.84 (4)	2.14 (5)	2.825 (4)	138 (4)

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

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1996); data reduction: SAINT and XPREP (Siemens, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1999); software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2066).

References

Bruker (1999). SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, X.-L., Niu, D.-Z. & Lu, Z.-S. (2007). Acta Cryst. E**63**, m2478.
Li, X. L., Tong, M. L., Niu, D. Z. & Chen, J. T. (2004). Chin. J. Chem. **22**, 64–68.
Li, X. L., Zhao, C. C., Chen, J. T. & Du, W. X. (2004). Chin. J. Chem. **22**, 533–536.
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
Siemens (1995). XPREP. Version 5.04. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supplementary materials

Bis(4-carboxypyridinium) aquapentakis(isothiocyanato-*κN*)iron(III) bis(pyridinium-4-carboxylate)

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Comment

Isothiocyanate anions exhibit a large variety of different coordination modes towards metal cations and, partially due to this, they are widely used as versatile ligands in many areas of coordination chemistry (Li, Tong *et al.*, 2004; Li, Zhao *et al.*, 2004 and Li *et al.*, 2007). Herein we describe the crystal structure of the iron(III) isothiocyanate complex [inaH]$_2$[Fe(H$_2$O)(NCS)$_5$].2[ina] (ina = isonicotinic acid).

A thermal ellipsoid drawing of the complex with the atomic numbering scheme is shown in Fig. 1. The iron complex lies on a mirror plane with the six-coordinated Fe^{III} ion, a coordinated water molecule and three of the five isothiocyanate ligands located directly within this plane (atoms Fe1, O1W, N1, C1, S1, N2, C2, S2, N4, C4 and S4). The coordination geometry around the Fe^{III} ion is slightly distorted octahedral. All the isothiocyanate anions coordinate to the iron(III) center through the nitrogen atoms in a slightly bent mode with C—N—Fe angles in the range of 150.7 (5)–166.8 (5)°. The ina molecules and the protonated inaH$^+$ cations interact with each other through N—H···O and O—H···O hydrogen bonds which leads to the formation of a 2-D layer perpendicular to the *b* axis. One of this sublayers is shown in Fig. 2. Each two of these layers sandwich another layer of {[Fe(H$_2$O)(NCS)$_5$]$^{2-}$}$_n$ anions with which they interact *via* electrostatic attraction and O—H···O hydrogen bonds, resulting in sheets of triple-layers perpendicular to the *b* axis. One of these triple-layers is shown in Fig. 3.

Experimental

AgNO$_3$ (0.51 g, 3.0 mmol), NH$_4$SCN (0.68 g, 4.5 mmol) and ina (1.11 g, 4.5 mmol) were added to a stirred solution of FeCl$_3$·6H$_2$O (0.41 g, 1.5 mmol) in water. The mixture was stirred at room temperature for 12 h. The solution was filtered and the filtrate was left to evaporate slowly in air. After a few days, purple-red crystals suitable for X-ray diffraction analysis were obtained.

Refinement

Water and N—H hydrogen atoms were located from the difference density Fourier maps and were refined with $U_{iso}(H) = 1.5U_{eq}(O)$ and $U_{iso}(H) = 1.2U_{eq}(N)$. All other H atoms were placed geometrically with C–H and O—H distances of 0.96 and 0.82 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$. Hydroxyl H atoms were allowed to rotate to best fit the experimental electron density.
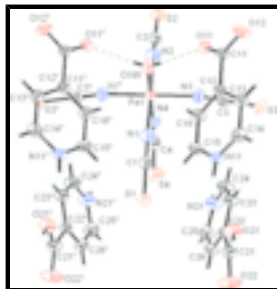
supplementary materials

Figures

Fig. 1. A view of the complex with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (v) x, $3/2 - y$, z.
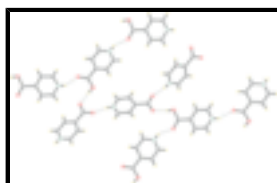

Fig. 2. The sublayer consisting of ina molcecules and inaH[+] cations. View along the b axis. Dashed lines represent N11—H11A⋯ O11[i], N21—H21A⋯O22[ii] and O21—H21⋯O12[i] hydrogen bonds. Symmetry codes: (i) $x + 1/2$, y, $-z + 1/2$; (ii) $x - 1/2$, y, $-z + 3/2$.

Fig. 3. The triple-layer seen along the c axis. Dashed lines represent hydrogen bonding interactions.

Bis(4-carboxypyridinium) aquapentakis(isothiocyanato-κ*N*)iron(III) bis(pyridinium-4-carboxylate)

Crystal data

$(C_6H_6NO_2)_2[Fe(NCS)_5(H_2O_1)]\cdot 2C_6H_5NO_2$	$F_{000} = 1756$
$M_r = 858.72$	$D_x = 1.519$ Mg m^{-3}
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 6815 reflections
$a = 14.8713$ (3) Å	$\theta = 1.9–25.1°$
$b = 21.0882$ (3) Å	$\mu = 0.74$ mm^{-1}
$c = 11.9741$ (2) Å	$T = 297$ (2) K
$V = 3755.18$ (11) Å^3	Prism, purple red
$Z = 4$	$0.36 \times 0.30 \times 0.20$ mm

Data collection

Siemens SMART CCD diffractometer	3405 independent reflections
Radiation source: fine-focus sealed tube	2589 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.043$
$T = 297(2)$ K	$\theta_{max} = 25.0°$
φ and ω scans	$\theta_{min} = 1.9°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -15 \rightarrow 17$
$T_{min} = 0.776$, $T_{max} = 0.866$	$k = -19 \rightarrow 25$
18247 measured reflections	$l = -12 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.132$	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 5.0802P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3405 reflections	$\Delta\rho_{max} = 0.71$ e Å^{-3}
265 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Fe1	0.04898 (5)	0.7500	0.46892 (6)	0.0447 (2)
S1	0.35902 (12)	0.7500	0.57736 (16)	0.0711 (5)
S2	−0.26880 (10)	0.7500	0.44506 (14)	0.0618 (4)
S3	0.11872 (8)	0.53111 (5)	0.42450 (10)	0.0666 (3)
S4	0.08889 (14)	0.7500	0.84926 (17)	0.0966 (7)
N1	0.1841 (3)	0.7500	0.4965 (4)	0.0642 (13)
N2	−0.0851 (3)	0.7500	0.4331 (5)	0.0666 (14)
N3	0.0549 (2)	0.65311 (16)	0.4608 (3)	0.0571 (9)
N4	0.0261 (4)	0.7500	0.6327 (4)	0.0671 (14)
C1	0.2566 (4)	0.7500	0.5337 (4)	0.0492 (13)
C2	−0.1609 (4)	0.7500	0.4375 (4)	0.0481 (13)
C3	0.0825 (3)	0.6021 (2)	0.4464 (3)	0.0476 (9)
C4	0.0520 (4)	0.7500	0.7235 (5)	0.0577 (15)
O1W	0.0739 (3)	0.7500	0.2978 (3)	0.0556 (11)
H1WA	0.079 (3)	0.718 (2)	0.268 (4)	0.083*
O11	0.08724 (13)	0.63784 (11)	0.1885 (2)	0.0400 (6)
O12	0.13720 (17)	0.57069 (15)	0.0600 (2)	0.0676 (9)

N11	0.41185 (19)	0.61060 (15)	0.2733 (3)	0.0465 (8)
H11A	0.468 (3)	0.6149 (18)	0.292 (3)	0.056*
C11	0.1473 (2)	0.60535 (16)	0.1433 (3)	0.0390 (8)
C12	0.24110 (19)	0.60742 (15)	0.1927 (3)	0.0348 (7)
C13	0.3076 (2)	0.56935 (17)	0.1478 (3)	0.0439 (9)
H13A	0.2943	0.5423	0.0888	0.053*
C14	0.3928 (2)	0.57152 (18)	0.1900 (3)	0.0500 (10)
H14A	0.4374	0.5456	0.1603	0.060*
C15	0.3498 (2)	0.64714 (18)	0.3203 (3)	0.0490 (9)
H15A	0.3652	0.6735	0.3796	0.059*
C16	0.2630 (2)	0.64613 (17)	0.2814 (3)	0.0451 (9)
H16A	0.2192	0.6714	0.3147	0.054*
O21	0.48392 (16)	0.57804 (13)	0.5311 (2)	0.0567 (7)
H21	0.5353	0.5759	0.5065	0.085*
O22	0.55326 (17)	0.58175 (18)	0.6951 (2)	0.0807 (10)
N21	0.2356 (2)	0.61800 (19)	0.7871 (3)	0.0648 (10)
H21A	0.185 (3)	0.622 (2)	0.817 (4)	0.078*
C21	0.4867 (2)	0.58419 (18)	0.6386 (3)	0.0479 (9)
C22	0.3962 (2)	0.59533 (15)	0.6907 (3)	0.0374 (8)
C23	0.3176 (2)	0.58314 (18)	0.6341 (3)	0.0471 (9)
H23A	0.3195	0.5671	0.5617	0.057*
C24	0.2371 (2)	0.5946 (2)	0.6843 (3)	0.0600 (11)
H24A	0.1837	0.5861	0.6469	0.072*
C25	0.3097 (3)	0.6308 (2)	0.8439 (3)	0.0625 (11)
H25A	0.3058	0.6477	0.9155	0.075*
C26	0.3918 (2)	0.61910 (18)	0.7975 (3)	0.0505 (9)
H26A	0.4442	0.6271	0.8376	0.061*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0430 (4)	0.0435 (4)	0.0475 (5)	0.000	0.0058 (3)	0.000
S1	0.0721 (11)	0.0533 (9)	0.0880 (12)	0.000	−0.0363 (9)	0.000
S2	0.0435 (8)	0.0693 (10)	0.0727 (11)	0.000	−0.0010 (7)	0.000
S3	0.0743 (8)	0.0469 (6)	0.0786 (8)	0.0132 (5)	−0.0133 (6)	0.0099 (5)
S4	0.0857 (13)	0.1384 (19)	0.0659 (12)	0.000	−0.0134 (10)	0.000
N1	0.052 (3)	0.069 (3)	0.071 (4)	0.000	−0.003 (3)	0.000
N2	0.046 (3)	0.070 (3)	0.084 (4)	0.000	−0.002 (3)	0.000
N3	0.071 (2)	0.045 (2)	0.055 (2)	−0.0017 (17)	0.0016 (17)	0.0027 (16)
N4	0.083 (4)	0.069 (3)	0.049 (3)	0.000	0.010 (3)	0.000
C1	0.065 (4)	0.040 (3)	0.043 (3)	0.000	0.001 (3)	0.000
C2	0.055 (4)	0.042 (3)	0.047 (3)	0.000	0.003 (3)	0.000
C3	0.049 (2)	0.053 (2)	0.041 (2)	−0.0067 (19)	−0.0052 (16)	0.0108 (17)
C4	0.049 (3)	0.060 (4)	0.064 (4)	0.000	0.012 (3)	0.000
O1W	0.078 (3)	0.038 (2)	0.050 (2)	0.000	0.011 (2)	0.000
O11	0.0217 (11)	0.0482 (14)	0.0502 (15)	0.0011 (10)	0.0022 (10)	−0.0036 (11)
O12	0.0392 (15)	0.085 (2)	0.078 (2)	0.0187 (14)	−0.0255 (14)	−0.0423 (17)
N11	0.0213 (14)	0.059 (2)	0.059 (2)	−0.0046 (14)	−0.0074 (14)	0.0054 (16)

C11	0.0261 (16)	0.046 (2)	0.045 (2)	0.0029 (15)	−0.0061 (15)	−0.0062 (16)
C12	0.0229 (15)	0.0407 (18)	0.0407 (19)	−0.0011 (13)	−0.0005 (13)	−0.0001 (14)
C13	0.0303 (17)	0.051 (2)	0.050 (2)	0.0044 (15)	−0.0023 (16)	−0.0119 (17)
C14	0.0283 (18)	0.056 (2)	0.066 (3)	0.0076 (16)	0.0033 (17)	−0.003 (2)
C15	0.0357 (18)	0.064 (2)	0.048 (2)	0.0000 (18)	−0.0113 (16)	−0.0103 (18)
C16	0.0301 (17)	0.058 (2)	0.047 (2)	0.0069 (16)	−0.0019 (15)	−0.0123 (17)
O21	0.0323 (13)	0.087 (2)	0.0512 (17)	0.0029 (13)	0.0102 (11)	0.0048 (14)
O22	0.0307 (15)	0.149 (3)	0.0622 (19)	0.0025 (16)	−0.0062 (14)	0.0092 (19)
N21	0.0378 (19)	0.093 (3)	0.064 (2)	0.0102 (18)	0.0123 (17)	−0.011 (2)
C21	0.0315 (19)	0.058 (2)	0.054 (2)	−0.0050 (16)	0.0036 (17)	0.0099 (18)
C22	0.0290 (17)	0.0373 (18)	0.046 (2)	−0.0035 (14)	0.0001 (14)	0.0040 (15)
C23	0.0335 (18)	0.064 (2)	0.044 (2)	−0.0017 (17)	0.0034 (16)	−0.0057 (18)
C24	0.031 (2)	0.092 (3)	0.058 (3)	−0.001 (2)	−0.0012 (18)	−0.007 (2)
C25	0.062 (3)	0.074 (3)	0.051 (2)	0.003 (2)	0.010 (2)	−0.018 (2)
C26	0.043 (2)	0.060 (2)	0.049 (2)	−0.0076 (17)	−0.0031 (17)	−0.0084 (18)

Geometric parameters (Å, °)

Fe1—N4	1.991 (5)	C12—C13	1.383 (4)
Fe1—N1	2.037 (5)	C13—C14	1.365 (5)
Fe1—N2	2.039 (5)	C13—H13A	0.9300
Fe1—N3	2.047 (3)	C14—H14A	0.9300
Fe1—N3[i]	2.047 (3)	C15—C16	1.373 (5)
Fe1—O1W	2.082 (4)	C15—H15A	0.9300
S1—C1	1.610 (6)	C16—H16A	0.9300
S2—C2	1.607 (6)	O21—C21	1.294 (4)
S3—C3	1.613 (4)	O21—H21	0.8200
S4—C4	1.602 (7)	O22—C21	1.201 (4)
N1—C1	1.167 (7)	N21—C25	1.323 (5)
N2—C2	1.129 (7)	N21—C24	1.325 (5)
N3—C3	1.164 (5)	N21—H21A	0.84 (4)
N4—C4	1.153 (7)	C21—C22	1.502 (5)
O1W—H1WA	0.76 (4)	C22—C26	1.375 (5)
O11—C11	1.249 (4)	C22—C23	1.375 (5)
O12—C11	1.246 (4)	C23—C24	1.361 (5)
N11—C14	1.325 (5)	C23—H23A	0.9300
N11—C15	1.327 (5)	C24—H24A	0.9300
N11—H11A	0.86 (4)	C25—C26	1.364 (5)
C11—C12	1.515 (4)	C25—H25A	0.9300
C12—C16	1.378 (5)	C26—H26A	0.9300
N4—Fe1—N1	90.5 (2)	C14—C13—H13A	120.0
N4—Fe1—N2	92.3 (2)	C12—C13—H13A	120.0
N1—Fe1—N2	177.2 (2)	N11—C14—C13	119.9 (3)
N4—Fe1—N3	93.10 (10)	N11—C14—H14A	120.1
N1—Fe1—N3	87.99 (10)	C13—C14—H14A	120.1
N2—Fe1—N3	91.85 (10)	N11—C15—C16	120.1 (3)
N4—Fe1—N3[i]	93.10 (10)	N11—C15—H15A	120.0
N1—Fe1—N3[i]	87.99 (10)	C16—C15—H15A	120.0

N2—Fe1—N3^i	91.85 (10)	C15—C16—C12	119.5 (3)
N3—Fe1—N3^i	172.64 (19)	C15—C16—H16A	120.3
N4—Fe1—O1W	179.6 (2)	C12—C16—H16A	120.3
N1—Fe1—O1W	89.1 (2)	C21—O21—H21	109.5
N2—Fe1—O1W	88.1 (2)	C25—N21—C24	122.6 (3)
N3—Fe1—O1W	86.88 (10)	C25—N21—H21A	120 (3)
N3^i—Fe1—O1W	86.88 (10)	C24—N21—H21A	117 (3)
C1—N1—Fe1	166.8 (5)	O22—C21—O21	125.6 (3)
C2—N2—Fe1	165.2 (5)	O22—C21—C22	120.7 (3)
C3—N3—Fe1	160.8 (3)	O21—C21—C22	113.6 (3)
C4—N4—Fe1	150.7 (5)	C26—C22—C23	119.1 (3)
N1—C1—S1	176.4 (5)	C26—C22—C21	119.1 (3)
N2—C2—S2	179.5 (6)	C23—C22—C21	121.8 (3)
N3—C3—S3	178.7 (4)	C24—C23—C22	119.7 (3)
N4—C4—S4	179.5 (6)	C24—C23—H23A	120.2
Fe1—O1W—H1WA	118 (4)	C22—C23—H23A	120.2
C14—N11—C15	122.1 (3)	N21—C24—C23	119.5 (4)
C14—N11—H11A	118 (3)	N21—C24—H24A	120.3
C15—N11—H11A	120 (3)	C23—C24—H24A	120.3
O12—C11—O11	125.6 (3)	N21—C25—C26	120.0 (4)
O12—C11—C12	116.1 (3)	N21—C25—H25A	120.0
O11—C11—C12	118.3 (3)	C26—C25—H25A	120.0
C16—C12—C13	118.4 (3)	C25—C26—C22	119.1 (3)
C16—C12—C11	122.3 (3)	C25—C26—H26A	120.4
C13—C12—C11	119.3 (3)	C22—C26—H26A	120.4
C14—C13—C12	120.0 (3)		

Symmetry codes: (i) x, $-y+3/2$, z.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H1WA⋯O11	0.76 (4)	1.95 (4)	2.711 (3)	178 (5)
N11—H11A⋯O11^{ii}	0.86 (4)	1.86 (4)	2.710 (3)	168 (4)
O21—H21⋯O12^{ii}	0.82	1.72	2.532 (3)	173
N21—H21A⋯O22^{iii}	0.84 (4)	2.14 (5)	2.825 (4)	138 (4)

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

Fig. 1

Fig. 2

Fig. 3