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Crystal structure, thermal and fluorescence properties of 2,2′:6′,2″-terpyridine-1,1′,1″-triium tetrachloridonickelate(II) chloride

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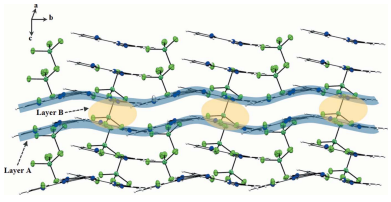
The title compound, $(C_{15}H_{14}N_3)[NiCl_4]Cl$, comprises an Ni^{II} cation tetrahedrally coordinated by four chloride anions, a non-coordinating chloride anion and an essentially planar terpyridinium trication ($tpyH_3^{3+}$), in which the central pyridinium ring forms dihedral angles of 5.7 (2) and 6.0 (2)° with the peripheral pyridinium rings. Three inter-species N—H···Cl hydrogen bonds are formed with the Cl^- anion, which also forms a link between the ($tpyH_3^{3+}$) cations through an aromatic C—H···Cl interaction, forming a zigzag chain extending along the 2_1 (*b*) screw axis. Two of the anionic Cl atoms of the $[NiCl_4]^{2-}$ anions form Ni—Cl···π interactions with separate pyridinium rings [Ni···*Cg* = 3.669 (3) and 3.916 (4) Å]. In the crystal, successive undulating inorganic and organic layers are formed, extending across the (100) plane. Thermogravimetric and differential thermal analysis (TGA/DTA) indicate that the compound starts to decompose at 313 K and may be a candidate for use as a blue-light luminescent material.

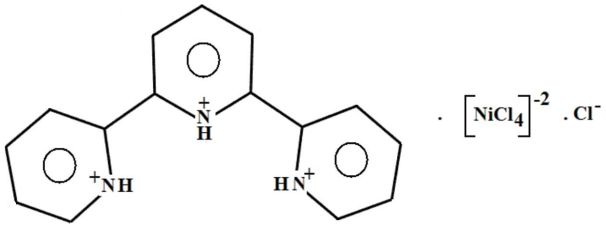
1. Chemical context

The 2,2′:6′,2″-terpyridine molecule (tpy) has been the object of numerous studies because of its excellent complexing properties on metal ions. The multitude of applications of this cation motivated a large development in the synthesis of terpyridines during the last decade. The compounds derived from the terpyridine molecule can be used in photochemistry for the realization of luminescent materials (Adeloye *et al.*, 2012), the assembly of electrochemical sensors (Indelli *et al.*, 1998), in photocatalysis (Mori *et al.*, 2012) and as a sensitizing agent in photovoltaic conversion processes (Kohle *et al.*, 1996). The literature reports some hybrid complexes of transition metal species incorporating tpy as a neutral ligand as well as complexes with its protonated forms [($tpyH^+$), ($tpyH_2^{2+}$), ($tpyH_3^{3+}$)] (Kochel, 2006). The title compound, which is a new hybrid complex, was characterized using IR spectroscopy and X-ray crystallography and its thermal and fluorescence properties have also been recorded.



2. Structural commentary

Crystals of $(C_{15}H_{14}N_3)[NiCl_4]Cl$, (I), are monoclinic (space group $P2_1$), the asymmetric unit comprising an organic terpyridinium ($tpyH_3^{3+}$) cation, a tetrachloronickelate(II) $[NiCl_4]^{2-}$ dianion and a free chloride anion (Cl5) (Fig. 1).



The ($tpyH_3^{3+}$) cation has the *cis–cis* conformation and is essentially planar, with dihedral angles between the central pyridine ring and the two peripheral ring moieties of the ligand of 5.7 (2) and 6.0 (2)°. The three protonated N atoms (N1, N2 and N3) form hydrogen bonds with the chloride counter-anion (Cl5) (Table 1), giving short H11···H22 and H22···H33 contacts (1.70 and 1.68 Å, respectively), which are comparable to those reported for $tpyH_3Cl(PF_6)_2$ (H···H range: 1.667–1.684 Å; Yoshikawa *et al.*, 2016). The complete protonation of an aromatic molecule that is nitrogen-enriched (a polynitrogenous derivative) is rarely observed, probably because of an unfavorable charge distribution resulting from the proximity of the nitrogen H atoms, as previously indicated in this structure. This results in an opening of the internal angles of the three N atoms [C1—N1—C5 = 124.0 (4), C10—N2—C6 = 118.9 (3) and C15—N3—C11 = 123.2 (3)°]. These values are comparable to those found in the literature for ($tpyH_3^{3+}$). In 2,2′:6′,2″-terpyridinetriium bis(hexafluoridophosphate) chloride (Yoshikawa *et al.*, 2016), C1—N1—C5 = 122.90, C6—N2—C10 = 117.60 and C11—N3—C15 = 123.27, C16—N4—C20 = 123.69, C21—N5—C25 = 118.22 and C26—N6—C30 = 123.97° and in *catena*-[(2,2′:6′,2″-terpyridinium)-(μ_3-sulfato)sulfatodioxouranium) nitrate dihydrate] (Jie Ling *et al.*, 2010), C1—N1—C5 = 123.33, C6—N2—C10 = 118.03 and C11—N3—C15 = 123.29°. The internal angles for a deprotonated terpyridine are C1—N1—C5 = 116.9 (8), C10—N2—C6 = 119.6 (11) and C15—N3—C11 = 117.1 (8)° (Maynard *et al.*, 2009).

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···Cl5	0.86	2.26	3.026 (4)	149
N2—H22···Cl5	0.86	2.67	3.532 (4)	178
N3—H33···Cl5	0.86	2.25	3.010 (4)	148
C14—H14···Cl5^{i}	0.93	2.78	3.421 (6)	127

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

The nickel(II) centre of the dianion has a quasi-regular tetrahedral environment [Ni—Cl bond length range, 2.185 (2)–2.201 (2) Å and Cl—Ni—Cl bond angle range, 108.08 (5)–111.59 (5)°] (Fig. 2). The interatomic distance and angle values are in good agreement with those taken from the literature (Igashira-Kamiyama *et al.*, 2013).

3. Supramolecular features

The previously described inter-species unit formed through the three individual N—H···Cl hydrogen bonds between the ($tpyH_3^{3+}$) cation and the $Cl5^-$ anion (Table 1) is extended through a C14—H14···Cl5^{i} hydrogen bond into chains extending along the 2_1 screw axis of the unit cell. Convoluted layers comprising successive [$tpyH_3^{3+}$, Cl^-] (type *A*) and $[NiCl_4]^{2-}$ (type *B*) ions extend across the (100) plane (Figs. 3 and 4). Two of the anionic Cl atoms of the $[NiCl_4]^{2-}$ anion form Ni—Cl···π interactions with separate pyridine ring moieties of the cation within the asymmetric unit: Ni1—Cl1···*Cg*1 = 3.916 (4) Å and Ni1—Cl2···*Cg*2 = 3.669 (3) Å, where *Cg*1 and *Cg*2 are the centroids of the N1/C1–C5 and N2/C6–C10 rings, respectively (Fig. 3).

4. Thermogravimetric analysis (TGA)

Thermal analyses were performed on a SETARM 92-16.18 PC/PG 1 instrument from 303 to 1273 K under a dynamic air

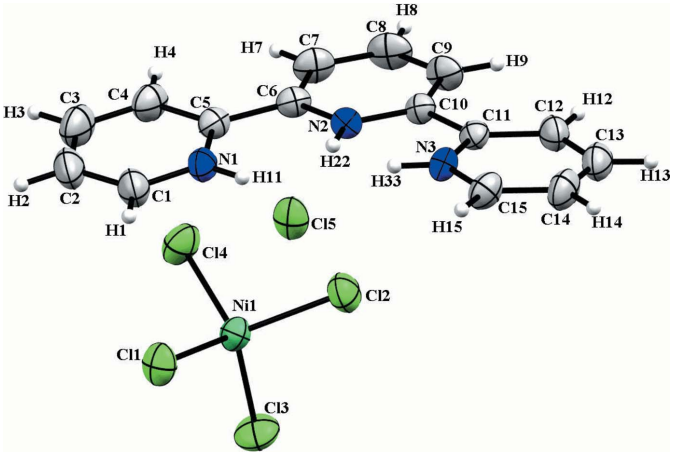


Figure 1
The asymmetric unit of $(C_{15}H_{14}N_3)[NiCl_4]Cl$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

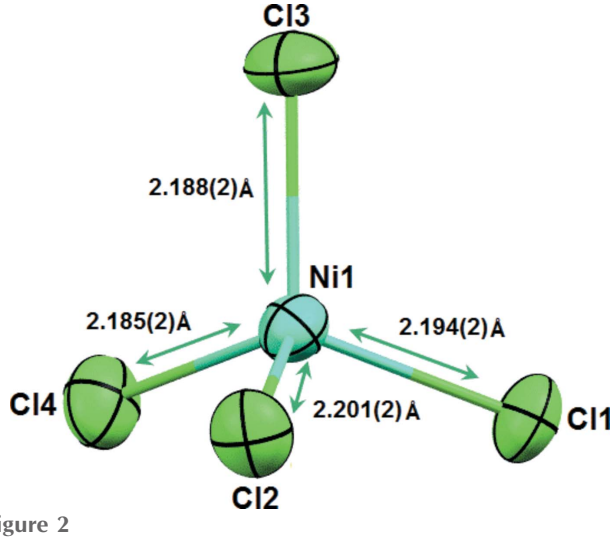


Figure 2
The nickel tetrahedral environment.

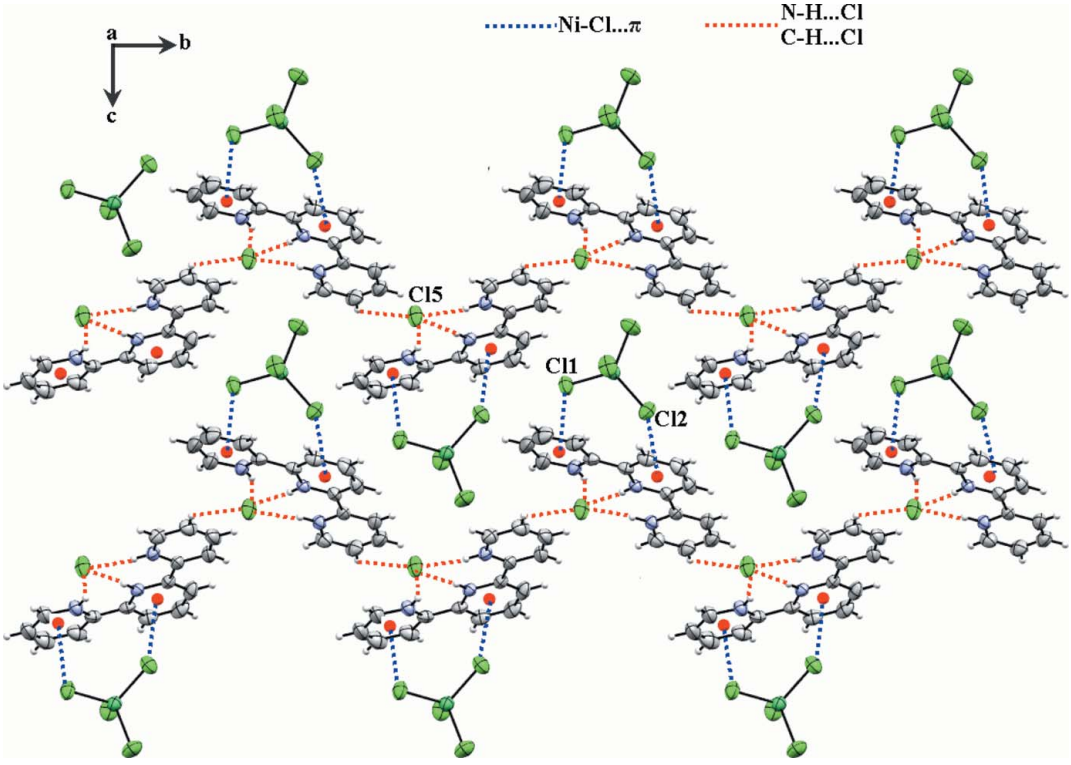


Figure 3
A view of the two-dimensional network of (I), showing the N—H···Cl and C—H···Cl hydrogen bonds (red dashed lines) and Ni—Cl···π interactions (blue dashed lines).

atmosphere and under nitrogen at 200.0 ml min^{-1} with a heating rate of 10 K min^{-1}.

The stability of the $(C_{15}H_{14}N_3)[NiCl_4]Cl$ complex was measured by TGA and the experimental results are in agreement with the calculated data. As shown in Fig. 5, the first weight loss of 16.5% (calculated 15.21%) at 40–126 K corresponds to the loss of the two coordinated chloride anions and the second loss of 48.6% (calculated 49.9%) at 126–281 K corresponds to the loss of the organic molecule $tpyH_3^{3+}$, and then the two coordinated and free chloride anions gradually

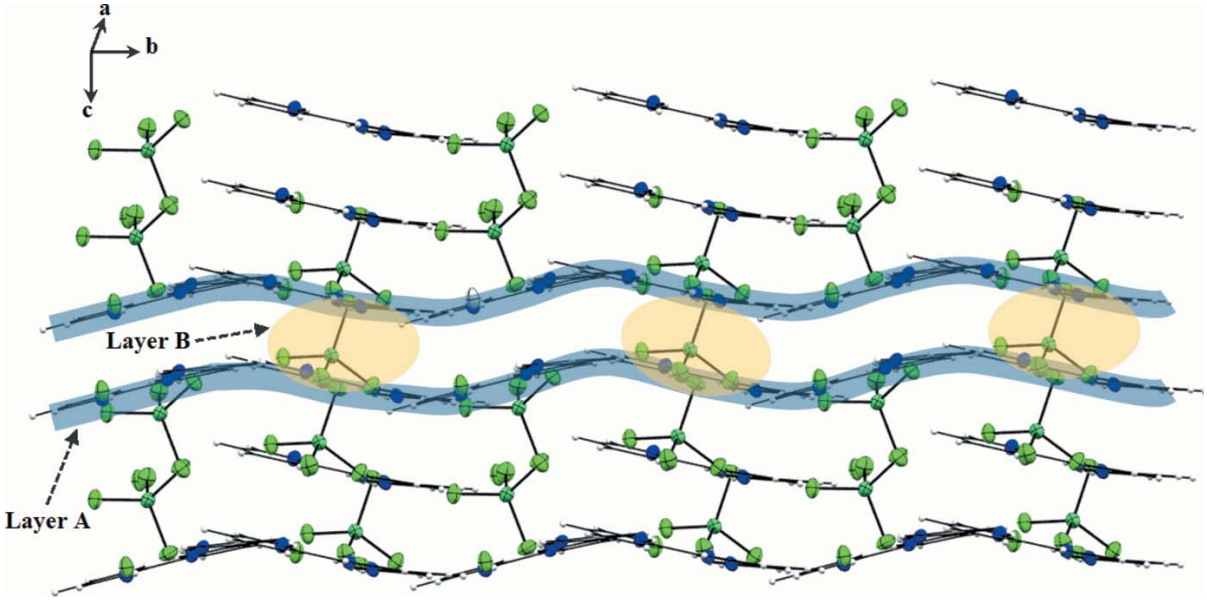


Figure 4
A perspective view of layers *A* and *B*.

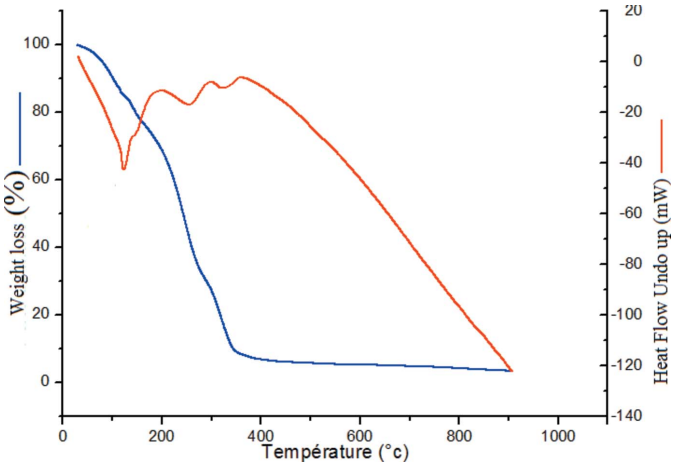


Figure 5
The thermogravimetric (TG) and differential thermal analysis (DTA) curves.

decompose ($\Delta P/P$ = 23.14%, calculated = 22.51%). In addition, the corresponding endothermic peaks (at 394.16; 554.63°C and at 638 K) in the differential scanning ATD curve also record the processes of weight loss.

5. Luminescent properties

Photoluminescence spectra were measured using a Cary Eclipse (Agilent Technologies) fluorescence spectrophotometer.

The fluorescence properties of $(C_{15}H_{14}N_3)[NiCl_4]Cl$ and the free ligand tpy were investigated in the solid state at 298 K. As depicted in Fig. 6, the new compound (I) exhibits fluorescence emission at *ca* 481 nm (excited at 250 nm) compared to that of tpy (425 nm, excited at 250 nm), which can be attributed to π–π^* electronic transitions. Thus, the title compound may be a candidate for use as a blue-light luminescent material and it is believed that more transition metal heterocyclic compounds with good luminescent properties may be developed (Wen *et al.*, 2007; Zhang *et al.*, 2010; Huang *et al.*, 2013).

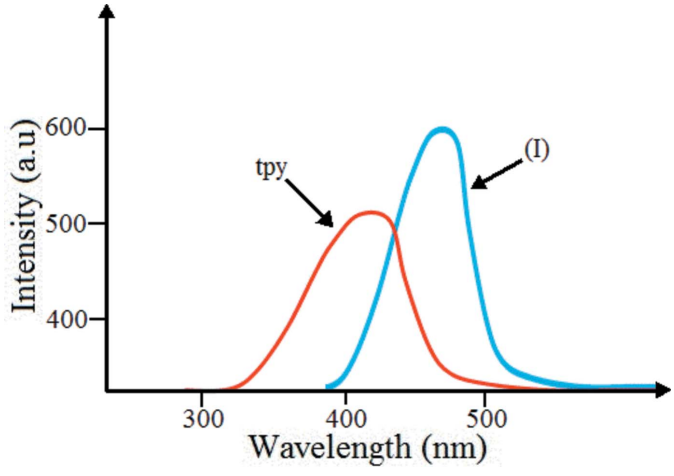


Figure 6
The solid-state fluorescence spectrum of tpy and the title compound (I) (excitation at 250 nm).

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_{15}H_{14}N_3)[NiCl_4]Cl$
M_r	472.25
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	293
a, b, c (Å)	6.689 (5), 13.809 (5), 10.620 (5)
β (°)	101.271 (5)
V (Å^3)	962.0 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.71
Crystal size (mm)	0.20 × 0.10 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	36239, 8772, 6308
R_{int}	0.031
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.828
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.150, 1.15
No. of reflections	8772
No. of parameters	218
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.51

Computer programs: *APEX2* and *SAINT* (Bruker, 2006), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *POVRay* (Persistence of Vision, 2004).

6. Database survey

A search of the Cambridge Structural Database (Version 5.38; Groom *et al.*, 2016) shows 4279 hits comprising the terpyridine species. However, only two structures containing the ($tpyH_3^{3+}$) form are present (Ling *et al.*, 2010; Yoshikawa *et al.*, 2016).

7. Synthesis and crystallization

All the chemicals and solvents were purchased commercially and used as received. The infrared spectra were recorded on a Perkin–Elmer spectrometer at room temperature in the range of 4000–500 cm^{-1}. tpy (1.67 g, 10 mmol) was dissolved in a 50/50 mixture of water and ethanol (20 ml) in a 50 ml round-bottom flask. Nickel(II) chloride (2.50 g, 10 mmol) was added to the flask to give a green-coloured solution that was stirred for 3 h under gentle heat, producing a green-coloured precipitate. The precipitate was filtered and washed twice with cold water/ethanol solvent then dried under vacuum for 20 min, producing a green powder (2.7g, 64% yield). Green prismatic crystals of the title complex (I) suitable for X-ray analysis were obtained from water/ethanol solvent. IR of (I) (cm^{-1}): 3390 (*v/s*), 2930 (*v/s*), 1667.8 (*s*), 1622.4 (*s*), 1417.4 (*m*), 987.6 (*w*), 540.6 (*w*).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed at calculated positions and refined as riding atoms, with C—H = 0.93 Å, N—H = 0.86 Å and with U_{iso}(H) = 1.2U_{eq}(C,N). Although not of relevance with this achiral molecule, the Flack parameter (Flack, 1983) was determined as 0.178 (16) for 4425 Friedel pairs. Minor non-merohedral twinning was identified and allowed for in the refinement, giving a BASF factor of 0.1783.

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Crystal structure, thermal and fluorescence properties of 2,2′:6′,2″-terpyridine-1,1′,1″-triium tetrachloridonickelate(II) chloride

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Computing details

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2008) and *POVRay* (Persistence of Vision, 2004).

(I)

Crystal data

$(C_{15}H_{14}N_3)[NiCl_4]Cl$
$M_r = 472.25$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 6.689$ (5) Å
$b = 13.809$ (5) Å
$c = 10.620$ (5) Å
$\beta = 101.271$ (5)°
$V = 962.0$ (9) Å^3
$Z = 2$
$F(000) = 476$
$D_x = 1.630$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6308 reflections
$\theta = 3.0$–$36.1°$
$\mu = 1.71$ mm^{-1}
$T = 293$ K
Prism, green
0.20 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
36239 measured reflections
8772 independent reflections
6308 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 36.1°$, $\theta_{min} = 3.0°$
$h = -11 \rightarrow 10$
$k = -22 \rightarrow 22$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.150$
$S = 1.15$
8772 reflections
218 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.6276P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2>2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.6965 (5)	0.0120 (2)	0.2808 (3)	0.0423 (8)
N2	0.6834 (4)	0.1969 (2)	0.2073 (2)	0.0345 (7)
N3	0.3276 (4)	0.2445 (2)	0.0620 (3)	0.0378 (8)
C1	0.6807 (7)	−0.0822 (3)	0.3068 (4)	0.0564 (14)
C2	0.8509 (9)	−0.1305 (4)	0.3730 (5)	0.0682 (16)
C3	1.0290 (9)	−0.0823 (4)	0.4081 (5)	0.0704 (16)
C4	1.0401 (7)	0.0151 (4)	0.3788 (4)	0.0570 (14)
C5	0.8694 (5)	0.0637 (3)	0.3144 (3)	0.0400 (9)
C6	0.8612 (5)	0.1667 (3)	0.2779 (3)	0.0377 (8)
C7	1.0221 (6)	0.2299 (4)	0.3166 (4)	0.0514 (13)
C8	0.9989 (6)	0.3259 (3)	0.2837 (5)	0.0566 (11)
C9	0.8147 (6)	0.3578 (3)	0.2109 (4)	0.0510 (11)
C10	0.6616 (5)	0.2905 (2)	0.1750 (3)	0.0360 (8)
C11	0.4595 (5)	0.3173 (2)	0.0989 (3)	0.0374 (8)
C12	0.3955 (7)	0.4115 (3)	0.0654 (4)	0.0493 (11)
C13	0.1989 (7)	0.4256 (3)	−0.0041 (4)	0.0555 (14)
C14	0.0724 (7)	0.3501 (4)	−0.0406 (4)	0.0574 (14)
C15	0.1389 (6)	0.2582 (3)	−0.0065 (4)	0.0496 (11)
Ni1	0.67429 (7)	0.12776 (3)	0.66208 (4)	0.0431 (1)
Cl1	0.53022 (16)	−0.01301 (7)	0.60866 (11)	0.0556 (3)
Cl2	0.55986 (17)	0.23114 (8)	0.50704 (10)	0.0576 (3)
Cl3	0.6050 (2)	0.18121 (10)	0.84272 (11)	0.0672 (4)
Cl4	1.00476 (14)	0.11245 (9)	0.68627 (12)	0.0629 (4)
Cl5	0.27653 (15)	0.03265 (7)	0.11437 (12)	0.0576 (3)
H1	0.55780	−0.11470	0.28090	0.0680*
H2	0.84260	−0.19570	0.39320	0.0820*
H3	1.14390	−0.11440	0.45200	0.0840*
H4	1.16290	0.04800	0.40240	0.0680*
H7	1.14480	0.20740	0.36450	0.0620*
H8	1.10530	0.36920	0.30980	0.0680*
H9	0.79550	0.42250	0.18730	0.0610*
H11	0.58970	0.04130	0.24020	0.0510*
H12	0.48240	0.46380	0.08890	0.0590*
H13	0.15350	0.48820	−0.02590	0.0670*
H14	−0.05810	0.36030	−0.08820	0.0690*
H15	0.05350	0.20540	−0.03080	0.0600*

H22	0.58510	0.15670	0.18310	0.0410*
H33	0.36610	0.18630	0.08330	0.0450*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0412 (14)	0.0405 (14)	0.0434 (14)	0.0049 (11)	0.0040 (11)	0.0059 (11)
N2	0.0329 (11)	0.0359 (12)	0.0329 (11)	−0.0041 (9)	0.0023 (9)	−0.0026 (10)
N3	0.0373 (13)	0.0349 (13)	0.0394 (13)	0.0067 (10)	0.0029 (10)	−0.0032 (10)
C1	0.069 (3)	0.044 (2)	0.057 (2)	0.0067 (19)	0.014 (2)	0.0092 (17)
C2	0.099 (4)	0.050 (2)	0.059 (2)	0.021 (3)	0.024 (3)	0.017 (2)
C3	0.067 (3)	0.081 (3)	0.061 (2)	0.032 (3)	0.007 (2)	0.016 (2)
C4	0.047 (2)	0.073 (3)	0.048 (2)	0.0178 (19)	0.0019 (16)	0.0088 (19)
C5	0.0381 (15)	0.0508 (18)	0.0295 (13)	0.0063 (14)	0.0024 (11)	0.0005 (12)
C6	0.0330 (13)	0.0479 (17)	0.0306 (13)	−0.0024 (12)	0.0024 (11)	−0.0055 (12)
C7	0.0339 (15)	0.069 (3)	0.0476 (19)	−0.0069 (16)	−0.0011 (14)	−0.0065 (18)
C8	0.0444 (19)	0.061 (2)	0.063 (2)	−0.0246 (17)	0.0074 (18)	−0.0163 (19)
C9	0.052 (2)	0.0391 (17)	0.064 (2)	−0.0166 (15)	0.0168 (18)	−0.0104 (16)
C10	0.0373 (14)	0.0345 (14)	0.0361 (14)	−0.0030 (11)	0.0070 (12)	−0.0056 (11)
C11	0.0431 (16)	0.0350 (14)	0.0352 (14)	0.0037 (12)	0.0106 (12)	−0.0022 (11)
C12	0.061 (2)	0.0354 (16)	0.053 (2)	0.0041 (15)	0.0147 (17)	0.0042 (14)
C13	0.068 (3)	0.050 (2)	0.0486 (19)	0.0185 (19)	0.0118 (18)	0.0102 (17)
C14	0.057 (2)	0.062 (3)	0.049 (2)	0.024 (2)	0.0004 (17)	0.0058 (18)
C15	0.0417 (18)	0.055 (2)	0.0487 (19)	0.0085 (15)	0.0002 (15)	−0.0056 (16)
Ni1	0.0447 (2)	0.0389 (2)	0.0450 (2)	0.0022 (2)	0.0074 (2)	−0.0037 (2)
Cl1	0.0557 (5)	0.0396 (4)	0.0668 (6)	−0.0065 (4)	0.0008 (4)	−0.0078 (4)
Cl2	0.0582 (6)	0.0542 (5)	0.0578 (5)	0.0045 (4)	0.0048 (4)	0.0156 (4)
Cl3	0.0789 (7)	0.0736 (7)	0.0531 (5)	0.0027 (6)	0.0231 (5)	−0.0196 (5)
Cl4	0.0395 (4)	0.0623 (7)	0.0851 (7)	0.0057 (4)	0.0075 (4)	−0.0053 (5)
Cl5	0.0413 (4)	0.0435 (5)	0.0823 (7)	−0.0114 (4)	−0.0017 (4)	0.0015 (5)

Geometric parameters (Å, º)

Ni1—Cl1	2.194 (2)	C7—C8	1.372 (7)
Ni1—Cl2	2.201 (2)	C8—C9	1.392 (6)
Ni1—Cl3	2.188 (2)	C9—C10	1.380 (5)
Ni1—Cl4	2.185 (2)	C10—C11	1.480 (5)
N1—C5	1.347 (5)	C11—C12	1.394 (5)
N1—C1	1.338 (5)	C12—C13	1.390 (7)
N2—C6	1.342 (4)	C13—C14	1.351 (7)
N2—C10	1.338 (4)	C14—C15	1.370 (7)
N3—C15	1.341 (5)	C1—H1	0.9300
N3—C11	1.344 (4)	C2—H2	0.9300
N1—H11	0.8600	C3—H3	0.9300
N2—H22	0.8600	C4—H4	0.9300
N3—H33	0.8600	C7—H7	0.9300
C1—C2	1.387 (7)	C8—H8	0.9300
C2—C3	1.352 (8)	C9—H9	0.9300

C3—C4	1.386 (8)	C12—H12	0.9300
C4—C5	1.384 (6)	C13—H13	0.9300
C5—C6	1.472 (6)	C14—H14	0.9300
C6—C7	1.384 (6)	C15—H15	0.9300

Cl1—Ni1—Cl4	109.13 (5)	N2—C10—C9	122.8 (3)
Cl1—Ni1—Cl2	108.08 (5)	N3—C11—C10	116.7 (3)
Cl1—Ni1—Cl3	111.59 (5)	N3—C11—C12	118.2 (3)
Cl3—Ni1—Cl4	108.20 (5)	C10—C11—C12	125.1 (3)
Cl2—Ni1—Cl3	109.57 (5)	C11—C12—C13	118.5 (4)
Cl2—Ni1—Cl4	110.28 (5)	C12—C13—C14	121.3 (4)
C1—N1—C5	124.0 (4)	C13—C14—C15	119.1 (4)
C6—N2—C10	118.9 (3)	N3—C15—C14	119.8 (4)
C11—N3—C15	123.2 (3)	N1—C1—H1	121.00
C5—N1—H11	118.00	C2—C1—H1	121.00
C1—N1—H11	118.00	C1—C2—H2	120.00
C10—N2—H22	121.00	C3—C2—H2	120.00
C6—N2—H22	121.00	C4—C3—H3	120.00
C15—N3—H33	118.00	C2—C3—H3	120.00
C11—N3—H33	118.00	C3—C4—H4	120.00
N1—C1—C2	118.8 (4)	C5—C4—H4	120.00
C1—C2—C3	119.7 (5)	C6—C7—H7	120.00
C2—C3—C4	119.9 (5)	C8—C7—H7	120.00
C3—C4—C5	120.4 (5)	C9—C8—H8	120.00
N1—C5—C4	117.2 (4)	C7—C8—H8	120.00
C4—C5—C6	125.7 (4)	C8—C9—H9	121.00
N1—C5—C6	117.2 (3)	C10—C9—H9	121.00
N2—C6—C5	115.5 (3)	C11—C12—H12	121.00
N2—C6—C7	121.5 (4)	C13—C12—H12	121.00
C5—C6—C7	123.0 (3)	C14—C13—H13	119.00
C6—C7—C8	119.4 (4)	C12—C13—H13	119.00
C7—C8—C9	119.4 (4)	C13—C14—H14	121.00
C8—C9—C10	118.0 (4)	C15—C14—H14	120.00
N2—C10—C11	115.1 (3)	C14—C15—H15	120.00
C9—C10—C11	122.1 (3)	N3—C15—H15	120.00

C5—N1—C1—C2	0.4 (6)	C4—C5—C6—N2	175.1 (3)
C1—N1—C5—C4	0.5 (5)	C4—C5—C6—C7	−7.0 (6)
C1—N1—C5—C6	179.7 (3)	N2—C6—C7—C8	0.9 (6)
C10—N2—C6—C5	177.3 (3)	C5—C6—C7—C8	−176.8 (4)
C10—N2—C6—C7	−0.7 (5)	C6—C7—C8—C9	−0.7 (7)
C6—N2—C10—C9	0.2 (5)	C7—C8—C9—C10	0.2 (6)
C6—N2—C10—C11	−179.1 (3)	C8—C9—C10—N2	0.1 (6)
C15—N3—C11—C10	179.5 (3)	C8—C9—C10—C11	179.3 (4)
C15—N3—C11—C12	0.8 (5)	N2—C10—C11—N3	−5.3 (4)
C11—N3—C15—C14	−0.8 (6)	N2—C10—C11—C12	173.4 (3)
N1—C1—C2—C3	−1.0 (7)	C9—C10—C11—N3	175.5 (3)
C1—C2—C3—C4	0.6 (8)	C9—C10—C11—C12	−5.9 (5)

C2—C3—C4—C5	0.4 (7)	N3—C11—C12—C13	0.1 (6)
C3—C4—C5—N1	−1.0 (6)	C10—C11—C12—C13	−178.5 (4)
C3—C4—C5—C6	179.9 (4)	C11—C12—C13—C14	−1.0 (6)
N1—C5—C6—N2	−4.0 (4)	C12—C13—C14—C15	1.0 (7)
N1—C5—C6—C7	173.9 (3)	C13—C14—C15—N3	−0.1 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···Cl5	0.86	2.26	3.026 (4)	149
N1—H11···N2	0.86	2.28	2.666 (4)	107
N2—H22···Cl5	0.86	2.67	3.532 (4)	178
N2—H22···N3	0.86	2.29	2.654 (4)	106
N3—H33···Cl5	0.86	2.25	3.010 (4)	148
C14—H14···Cl5^{i}	0.93	2.78	3.421 (6)	127

Symmetry code: (i) −*x*, *y*+1/2, −*z*.