Synthesis, crystal structure and magnetic properties of bis(5,5′-dimethyl-2,2′-bipyridine-κ^2N,N')-(acetato-κ^2O,O') nickel(II) perchlorate hydrate

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Abstract

The ionic complex [Ni(5,5'-*dmbpy*)$_2$(*ac*)]ClO$_4$·H$_2$O (**1**; 5,5'-*dmbpy* = 5,5'-dimethyl-2,2'-bipyridine; *ac* = acetato) was isolated as violet crystals from the aqueous-ethanolic system nickel acetate – 5,5'-*dmbpy* – KClO$_4$. Within the complex cation the Ni(II) atom is hexacoordinated by two chelating 5,5'-*dmbpy* ligands and one chelating *ac* ligand. The mean Ni—N and Ni—O bonds are 2.0628 (17) and 2.1341 (15) Å, respectively. The water solvate molecule is disordered over two partially occupied positions; the solvate water molecule links two complex cations and two perchlorate anions into hydrogen bonded centrosymmetric dimers, which are futher connected by π-π interactions. The magnetic properties of complex **1** at low temperatures are governed by the action of single-ion anisotropy, *D*, which arises from the reduced local symmetry of the *cis*-NiO$_2$N$_4$ chromophore. The fitting of the variable temperature magnetic data (2 - 300 K) yielded the following magnetic parameters: g$_{iso}$ = 2.134, D/hc = 3.13 cm^{-1}, c_{TIM} = 0.92 × 10^{-9} m^3 mol^{-1}, zj/hc = -0.15 cm^{-1}.

1. Introduction

The magnetic properties of coordination compounds continue to be the focus of important research in inorganic chemistry. Coordination complexes of Ni(II) are still the object of studies with varied objectives, including studies of the magneto-structural correlation between the zero field splitting parameter, *D* and the geometric parameters of the Ni(II) coordination polyhedron (Boča, 2004; Ivaníková *et al.*, 2006; Costes *et al.*, 2012; Maganas *et al.*, 2012). Within our broader study of Ni(II) complexes as magnetic materials (Černák *et al.*, 2012; Černák *et al.*, 2009; Kočanová *et al.*, 2010), we have undertaken a study of the system Ni(II) – 5,5'-*dmbpy* – *ac* – ClO$_4^-$ from which the title complex [Ni(5,5'-*dmbpy*)$_2$(*ac*)]ClO$_4$·H$_2$O (**1**; 5,5'-*dmbpy* = 5,5'-dimethyl-2,2'-bipyridine, *ac* = acetato) was isolated. We report here its synthesis, crystal structure and magnetic properties.

2. Experimental

Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O analyzer. Infrared spectra in the range of 4000 – 400 cm^{-1} were recorded on a Perkin Elmer Spectrum 100 CsI DTGS FT—IR Spectrophotometer with a UATR 1 bounce-KRS-5 accessory. The TG and DTA curves of dehydration were recorded on a Netzch STA 409 PC/PG instrument under the following conditions: sample weight = 52.354 mg, heating rate = 9°/min, dynamic air atmosphere, temperature range 30-250 °C, aluminium oxide crucible.

The susceptibility of the powdered sample of the title complex was measured using SQUID magnetometer (MPMS, Quantum Design). A magnetic field *B* = 0.1 T was applied during the susceptibility measurement and the background contribution arising from the varnish, gelcap and straw is negligible below 20 K. The obtained values of magnetic susceptibility were corrected for diamagnetic contribution using Pascal constants (Carlin, 1986).

2.1. Synthesis and crystallization

Ni(CH$_3$COO)$_2$·4H$_2$O, KClO$_4$, 5,5'-dimethyl-2,2'-bipyridine and ethanol (96%) were purchased from commercial sources and used as received. Warning: the perchlorates are potentially explosives so should be handled with caution, so the syntheses should be carried out using small quantities.

A warm solution of 5,5'-*dmbpy* [1.00 mmol, 0.184 g in 25 cm^3 of ethanol (96%)], was added with stirring to a hot (about 80 °C) aqueous solution of Ni(CH$_3$COO)$_2$·4H$_2$O (1 mmol, 0.249 g, in 10 cm^3 of water), followed by addition of solid KClO$_4$ (1 mmol, 0.139 g). The resulting blue solution was filtered and allowed to sit at room temperature. Within three days light violet plates of **1** were obtained, which were collected by filtration, quickly washed with a small volume of water and dried in air. Yield: 45%. Analyses (CHNOS Elemental Analyzer vario MICRO, exp./calc.) [%]: C: 50.31/51.73; H: 4.40/4.84; N: 8.87/9.28.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms attached to aromatic C atoms were placed at calculated positions (C—H 0.95 Å) and refined as riders. Methyl H atoms were placed in geometrically idealized positions (C—H 0.98 Å) with the starting value of the torsion angle about the vicinal C—C bond determined from a local difference Fourier calculation. During refinement the methyl groups were permitted to rotate but not to tilt. The U(iso) values of H atoms were set to xU(eq) of their respective parent atoms with x = 1.5 for methyl hydrogen atoms and x = 1.2 for all others. The locations of the H atoms of the five independent methyl groups were checked at the end of refinement using omit maps.

Two atomic sites located at less than 1 Å from each other were assigned as partially occupied water oxygen atoms O7A and O7B and were refined with independent positional and common anisotropic displacement parameters; their occupancies were initially constrained to sum to 1.0. The resulting convergent value of the population parameter gave site occupation factors of 0.670 (5) for O7A and 0.330 (5) for O7B. Several models with slight variations in the treatment of the site occupancies result in credible displacement parameters, including models with partial (but nearly complete) total occupancy. The final value of the O7A···O7B distance is 0.871 (9) Å. No anti-bumping restraints were applied. The H atoms of these water sites were located through a combination of difference Fourier maps and hydrogen-bonding considerations. The O—H and H···H distances were restrained to values of 0.88 (1) and 1.33 (2) Å, respectively. In addition, similarity restraints were used for the O—H and vicinal H···H distances. For these H atoms, Uiso was set to 1.5Ueq(O).

3. Results and discussion

From the aqueous-ethanolic system nickel acetate – 5,5'-*dmbpy* – KClO$_4$ (molar ratio 1:2:1), the title complex **1** was isolated in the form of violet crystals. The same product was also prepared starting from a mixture of nickel acetate and nickel perchlorate in 1:1 molar ratio. The syntheses were reproducible. The products were characterized by elemental analysis (see the experimental part) and by thermal analysis of their dehydration. The thermal analysis of **1** showed that a weakly endothermic dehydration occurs in the temperature range 46 - 128 °C, and the observed mass loss of 2.63 % is in good agreement with the calculated value of 2.98 %.

A search of the CSD (V 5.35 through Update 3; Allen, 2002; Bruno *et al.*, 2002), yielded only two other complexes of Ni(II) containing the 5,5'-*dmbpy* ligand whose structures have been reported to date, namely [Ni(5,5'-*dmbpy*)$_2$(N$_3$)$_2$]·H$_2$O (Phatchimkun *et al.*, 2009) and [{Ni(5,5'-*dmbpy*)N$_3$}$_2$(N$_3$)$_2$] (Hou, 2008). It is worth noting that the crystal structure of the analogous complex [Ni(*bpy*)$_2$(*ac*)]ClO$_4$·2H$_2$O (**2**) has been reported (Holz *et al.*, 1996) but that, surprisingly, no other Ni(II) complex with *bpy* and chelating acetato ligands has been struturally characterized. In addition, two other

complexes of Ni(II) with *bpy* and *ac* ligands are known; however, in [Ni(*bpy*)(*ac*)$_2$(H$_2$O)$_2$] (Ye *et al.*, 1998) *ac* is coordinated in a unidentate fashion and in [Ni$_2$(*bpy*)$_2$(*ac*)$_3$(*aha*)]·CH$_3$CH$_2$OH (*aha* is acetohydroxamato) *ac* ligands act simultaneously as unidentate and *syn-syn* bridging ligands (Jedner *et al.*, 2002).

The crystal structure of **1** is ionic and is composed of [Ni(5,5'-*dmbpy*)$_2$(*ac*)]$^+$ complex cations, perchlorate anions and water molecules of crystallization (Fig. 1, Table 2). The central Ni(II) atom in the complex cation is hexacoordinated by a *cis*-O$_2$N$_4$ donor set. Four coordination sites are occupied by two chelating 5,5'-*dmbpy* ligands and the 5th and 6th coordination sites, mutually *cis*, are occupied by a chelating acetato ligand. The same type of coordination of the Ni(II) atom was observed previously in the analogous [Ni(*bpy*)$_2$(*ac*)]ClO$_4$·2H$_2$O (Holz *et al.*, 1996) and in the similar complex [Ni(*bpy*)$_2$(*mal*)]·7.34H$_2$O with a chelating maleato (*mal*) ligand (Pavlová *et al.*, 2008).

The Ni—N bond distances in **1** span the narrow range of 2.0510 (17) - 2.0784 (17) Å (Table 2) and are comparable with the average value of 2.0889 (13) Å found in [Ni(5,5'-*dmbpy*)$_2$(N$_3$)$_2$]·H$_2$O (Phatchimkun *et al.*, 2009). The Ni—O bond lengths, in contrast, are 2.1268 (14) and 2.1414 (15) Å, indicating weak asymmetry of the chelate bonding of the *ac* ligand, similar to what was found for **2** (Holz *et al.*, 1996). The observed Ni—O bonds are longer than the Ni—O bonds in the case of *syn-syn* bridging [average value 2.049 (3) Å] (Jedner *et al.*, 2002); the longer distance may be the consequence of internal strain in the four-membered metallacycle as reflected by the sharp bite angle of 61.87 (5)° (Table 2). The remaining geometric parameters in **1** associated with the ligands are unremarkable (Deng *et al.*, 2012; Berenguer *et. al.* 2009), as is the geometry of the perchlorate counterion.

The uncoordinated water molecule is disordered over two partially occupied positions O7A and O7B, whose site occupancy factors were refined with a total-population constraint to unity, giving occupancies of 0.670 (5) and 0.330 (5) for O7A and O7B, respectively. As calculated by Platon (Spek, 2009), the water sites occupy a void of volume 52 Å^3 around the inversion center at (1/2,1/2,1/2). A water molecule involved in hydrogen bonding may occupy a volume of about 40 Å^3 (29.9 Å^3/molecule in ice at 4 °C) and because of the center of symmetry our model places two water molecules in the void. Except for the impossibly short O7A···O7B contact (obviated by partial occupancies), all of the other unique O···O and C—H···O contacts in this region (Table 3) have acceptable geometries. The displacement tensors for the O7A and O7B sites are larger than those for the rest of the structure, but not excessively so; and that for O7A is prolate. We take these results to be a reflection of the space available to these water molecules and of the weak nature of their non-covalent interactions (Table 3).

One of the possible sets of intermolecular interactions involving the disordered water sites and the neighboring cations and anions is shown in Figure 2, along with one of the alternative patterns, shown in gray. Neither of these two patterns involves a direct or singly bridged non-bonded interaction between the two inversion related cations of **1**. As can be seen from Table 3, the contacts involved, even those that can be categorized as hydrogen bonds, are not strong in any case. The dimeric aggregate shown in Figure 2 is further extended through non-bonded C—H···O contacts involving C2—H2 and C20—H20, with acetate O atoms of the cation as receptors. These contacts, which together mediate the formation of a chain parallel to [10$\bar{1}$], could in principle be classified as non-classical hydrogen bonds, albeit weak ones, according to the current IUPAC definition of that term (Arunan *et al.*, 2011ab, Desiraju, 2011). More convincing non-classical H-bonds, with C3—H3 and C21—H21 as donors, have O atoms of neighboring perchlorate ions as acceptors.

In addition to their weak C—H···O interactions, the cations of **1** are involved in more significant π···π contacts to the same neighbors. Using Cg1 to denote the centroid of the pyridyl ring containing N1, and Cg2 for that containing N2, Cg1···Cg2^{ii} is 3.5627 (12) Å and the perpendicular distance from Cg1 to the ring containing Cg2^{ii} is 3.3155 (9) Å. With a dihedral angle of 1.61 (10)° between the rings, the perpendicular distance from Cg2^{ii} to the ring of Cg1 is slightly different, 3.3348 (8) Å. Using Cg3 and Cg4 for the centroids of the pyridyl rings containing N3 and N4, Cg3···Cg4^{iv} is

3.6639 (13) Å and the perpendicular distances from Cg3 and Cg4[iv] to the planes of their respective contacting rings are 3.3285 (9) and 3.4649 (9) Å [dihedral angle 5.94 (11)°]. [Symmetry codes (ii): -x+2, -y, -z+1; (iv): -x+1, -y, -z+2.] Figure 3 shows the resulting zig-zag chain aggregate parallel to $[10\bar{1}]$. Neighboring chains interact weakly through C—H$\cdots\pi$ interactions, shown in blue in Figure 3, which are perhaps best classified as Debye forces (weak dipole - induced dipole).

The broad absorption band of medium intensity positioned at 3450 cm^{-1} in the IR spectrum of complex **1** (see Supplementary material) is in line with the presence of water molecules which are involved in hydrogen bonding inter-actions (bathochromic shift). Several weak absorption bands observed in the range 3115 - 3028 cm^{-1} and 2980 - 2748 cm^{-1} were assigned to C—H streching vibrations associated with aromatic and aliphatic carbon atoms, respectively. The most intense absorption band in the IR spectrum of **1** is at 1109 cm^{-1} and indicates the presence of the perchlorate anion (Nakamoto, 1997). Within the rather broad region 1576 - 1394 cm^{-1} several bands can be observed. This region is typical for absorptions arising from C—N, C—C and carboxylate stretching vibrations, but their unambigous assignment is difficult.

Regarding the magnetic properties of complex **1**, the temperature dependence of the product function (Fig. 4) shows an almost linear decrease from the room temperature value $\chi T / C_0 = 3.10$ down to $T = 25$ K. Note that $\chi T /(C_0)_{HT} = g^2_{Ni}S_{Ni}(S_{Ni} + 1) / 3 = 2.94$. The subsequent drop below 25 K is caused by zero-field splitting, and the tendency to approach zero at zero temperature indicates easy plane anisotropy ($D > 0$). The inverse susceptibility shows an almost linear progression with a negative value of the Weiss constant ($\Theta < 0$) when the Curie-Weiss law is applied.

For fitting the magnetic data a zero-field splitting Hamiltonian is appropriate (see Equation 1) which yields the following set of magnetic parameters: g$_{iso}$ = 2.134, D/hc = 3.13 cm^{-1}, χ_{TIM} = 0.92 × 10^{-9} m^3 mol^{-1}, zj/hc = -0.15 cm^{-1} (R = 0.014). The g-factor adopts an expected value for mononuclear Ni(II) complexes and the value of the D-parameter is also typical for hexacoordinate, quasioctahedral Ni(II) systems with the *cis*-{NiO$_2$N$_4$} chromophore. With $D > 0$, the ground state possesses $M_S = 0$ and it is nonmagnetic. Owing to a rather low D-value, the g-factor anisotropy has not been considered in fitting the magnetic susceptibility data. The small negative value of the molecular-field correction (zj) confirms the presence of exchange interactions of an antiferromagnetic nature in the solid state.

Table 1

Experimental details

Crystal data	
Chemical formula	C$_{26}$H$_{27}$N$_4$NiO$_2$$^+$·ClO$_4$$^-$·H$_2$O
M_r	603.69
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	110
a, b, c (Å)	10.8804 (3), 11.4335 (3), 12.5387 (3)
α, β, γ (°)	66.319 (2), 78.224 (2), 69.035 (2)
V (Å^3)	1330.59 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.88
Crystal size (mm)	0.20 × 0.14 × 0.07
Data collection	
Diffractometer	Xcalibur, Sapphire3 diffractometer

Absorption correction	Multi-scan
	Multi-scan SCALE3 ABSPACK (Agilent Technologies, 2011)
T_{min}, T_{max}	0.855, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31626, 6083, 5416
R_{int}	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650

Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.093, 1.08
No. of reflections	6083
No. of parameters	370
No. of restraints	12

H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.72, −0.45

Computer programs: *CrysAlis PRO* (Agilent Technologies,2011) Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET), *SIR97* (Altomare *et al.*, 1994), *SHELXL2014*/7 (Sheldrick, 2015), Diamond (Brandenburg,2007), *publCIF* (Westrip, 2010).

Table 2

Hydrogen-bond geometry (Å, º) for (1)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7A—H1$W\cdots$O4	0.89 (1)	2.19 (1)	2.971 (5)	147 (2)
O7B—H1$W\cdots$O4	0.89 (1)	2.19 (1)	3.011 (10)	153 (2)
O7A—H2$W\cdots$O2	0.89 (1)	2.13 (1)	2.974 (5)	159 (3)
O7B—H3$W\cdots$O7A^{i}	0.89 (1)	2.33 (5)	3.144 (12)	152 (11)
O7B—H3$W\cdots$O7B^{i}	0.89 (1)	2.46 (10)	3.19 (2)	140 (12)
C2—H2$\cdots$O1^{ii}	0.95	2.52	3.376 (3)	151
C3—H3$\cdots$O5^{iii}	0.95	2.37	3.285 (3)	161
C5—H5$\cdots$O2	0.95	2.64	3.198 (3)	118
C20—H20$\cdots$O2^{iv}	0.95	2.56	3.421 (3)	152
C21—H21$\cdots$O4^{iv}	0.95	2.33	3.267 (3)	169
C23—H23$\cdots$O1	0.95	2.60	3.158 (3)	118

| C23—H23···O5^{v} | 0.95 | 2.60 | 3.187 (3) | 120 |
| C26—H26A···O7B^{i} | 0.98 | 2.44 | 3.334 (11) | 151 |

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

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Figure 1

Asymmetric unit of **1** along with the atom numbering scheme. Water sites O7A and O7B are partially occupied (see text). Displacement ellipsoids are drawn at the 50% probability level.

Figure 2

One of the possible schemes of H-bonding and other contacts in **1** (dashed lines). Hydrogen atoms not involved in H-bonds are omitted for clarity [symmetry code: (i) - x + 1, -y + 1, - z + 1]. One of the possible alternatives involving disordered congeners of O7A and O7B is shown in gray. The 5,5'-dmbpy H atoms shown, H2 and H20, are those that contact symmetry relatives of O1 and O2, extending the structure in the [1$\bar{1}$0] and [0$\bar{1}$1] directions.

Figure 3

Self-complementary pairs of π···π interactions in 1 (dashed red lines), which join the cations into zigzag aggregates. Weak C—H···π contacts are shown as dashed blue lines. "*Cg*" labels alongside methylpyridyl rings refer to the centers of gravity of those rings. Perchlorate anions and free water have been omitted. Symmetry codes: (ii) -x + 2, -y, -z + 1; (iv) -x + 1, -y, -z + 2; (v) -x + 2, -y, -z + 2.

Figure 4

Magnetic data for **1**: left – temperature dependence of the dimensionless product function (inset: molar magnetic susceptibility per formula unit); right – inverse magnetic susceptibility. Gray circles – experimental data, solid lines – fitted.

supplementary materials

supplementary materials

Synthesis, crystal structure and magnetic properties of bis(5,5′-dimethyl-2,2′-bipyridine-*κ²N,N*)-(acetato-*κ²O,O*) nickel(II) perchlorate hydrate

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Computing details

Data collection: *CrysAlis PRO* (Agilent Technologies,2011) Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET); cell refinement: *CrysAlis PRO* (Agilent Technologies,2011) Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET); data reduction: *CrysAlis PRO* (Agilent Technologies,2011) Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015); molecular graphics: Diamond (Brandenburg,2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

bis(5,5′-dimethyl-2,2′-bipyridineκ²N,N′)- (acetato-κ²O,O′) nickel(II) perchlorate hydrate (0.9)

Crystal data

$C_{26}H_{27}N_4NiO_2^+ \cdot ClO_4^- \cdot H_2O$	$Z = 2$
$M_r = 603.69$	$F(000) = 628$
Triclinic, $P\overline{1}$	$D_x = 1.507$ Mg m^{-3}
$a = 10.8804$ (3) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.4335$ (3) Å	Cell parameters from 16444 reflections
$c = 12.5387$ (3) Å	$\theta = 4.2$–30.7°
$\alpha = 66.319$ (2)°	$\mu = 0.88$ mm^{-1}
$\beta = 78.224$ (2)°	$T = 110$ K
$\gamma = 69.035$ (2)°	Plate, violet
$V = 1330.59$ (7) Å^3	$0.20 \times 0.14 \times 0.07$ mm

Data collection

Xcalibur, Sapphire3 diffractometer	31626 measured reflections
Radiation source: sealed X-ray tube	6083 independent reflections
Detector resolution: 16.0655 pixels mm^{-1}	5416 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.035$
Absorption correction: multi-scan Multi-scan SCALE3 ABSPACK (Agilent Technologies, 2011)	$\theta_{max} = 27.5°$, $\theta_{min} = 4.2°$
	$h = -14\rightarrow14$
	$k = -14\rightarrow14$
	$l = -16\rightarrow16$
$T_{min} = 0.855$, $T_{max} = 1.000$	

Refinement

Refinement on F^2	12 restraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.036$	
$wR(F^2) = 0.093$	Hydrogen site location: mixed
$S = 1.08$	H-atom parameters constrained
6083 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.5035P]$
370 parameters	where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.72$ e Å^{-3}

$\Delta\rho_{min} = -0.45$ e Å^{-3}

Special details

Experimental. Elemental analysis was performed on CHNOS Elemental Analyzer vario MICRO instrument. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT—IR Spectrophotometer with UATR accessory in the range of 4000–400?cm-1. IR (in cm^{-1}): 3554 sh, 3483 m, 3427 m, 3115 w, 3064 w, 3047 sh, 3028 w, 2980 w, 2960 w, 2928 w, 2872 w, 2847 w, 2748 w, 2794 w, 1641 w,1608 m, 1601 sh, 1587 m, 1576 m, 1537 s, 1502 m, 1481 s, 1454 s, 1421 sh, 1394 m, 1346 sh, 1317 m, 1294 w, 1250 w, 1234 m, 1167 w, 1149 m, 1109 vs, 1098 sh, 1084 vs, 1049 s, 999 m, 974 w, 937 w, 849 s, 833 s, 818 w, 762 w, 731 m, 694 w, 677 m, 652 m, 620 s, 553 w, 540 w, 496 w, 484 sh, 422 m.

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.74173 (2)	0.00664 (2)	0.73994 (2)	0.01468 (8)	
Cl1	0.77635 (5)	0.49449 (5)	0.76694 (4)	0.02327 (12)	
O1	0.65942 (14)	0.02326 (15)	0.59259 (12)	0.0201 (3)	
O2	0.55764 (14)	0.15889 (15)	0.68879 (13)	0.0221 (3)	
O3	0.76577 (19)	0.50234 (18)	0.88070 (14)	0.0355 (4)	
O4	0.68946 (19)	0.42413 (19)	0.76736 (17)	0.0392 (4)	
O5	0.73810 (17)	0.62781 (16)	0.68170 (14)	0.0306 (4)	
O6	0.90982 (17)	0.42330 (19)	0.73845 (15)	0.0359 (4)	
O7A	0.4688 (4)	0.4515 (5)	0.6443 (5)	0.0750 (11)	0.670 (5)
H1W	0.529 (3)	0.4774 (18)	0.659 (4)	0.113*	
H2W	0.510 (4)	0.3641 (12)	0.668 (6)	0.113*	0.670 (5)
O7B	0.4626 (9)	0.5364 (10)	0.6152 (10)	0.0750 (11)	0.330 (5)
H3W	0.507 (7)	0.545 (12)	0.546 (2)	0.113*	0.330 (5)
N1	0.85437 (17)	0.12639 (17)	0.63477 (14)	0.0168 (3)	
N2	0.92407 (16)	−0.13710 (17)	0.73759 (14)	0.0162 (3)	
N3	0.75971 (16)	0.02205 (16)	0.89466 (14)	0.0162 (3)	
N4	0.64260 (16)	−0.12145 (17)	0.85625 (14)	0.0166 (3)	
C1	0.9822 (2)	0.0611 (2)	0.61426 (17)	0.0177 (4)	
C2	1.0686 (2)	0.1309 (2)	0.54360 (18)	0.0222 (4)	
H2	1.1585	0.0840	0.5300	0.027*	
C3	1.0219 (2)	0.2696 (2)	0.49320 (18)	0.0241 (4)	
H3	1.0802	0.3184	0.4452	0.029*	
C4	0.8900 (2)	0.3377 (2)	0.51278 (18)	0.0222 (4)	
C5	0.8108 (2)	0.2602 (2)	0.58515 (17)	0.0207 (4)	
H5	0.7205	0.3048	0.6002	0.025*	
C6	0.8331 (3)	0.4873 (2)	0.4580 (2)	0.0294 (5)	
H6A	0.8079	0.5267	0.5188	0.044*	
H6B	0.7550	0.5090	0.4178	0.044*	
H6C	0.8991	0.5239	0.4017	0.044*	
C7	1.02135 (19)	−0.0865 (2)	0.67171 (16)	0.0168 (4)	
C8	1.1489 (2)	−0.1704 (2)	0.66115 (18)	0.0216 (4)	
H8	1.2157	−0.1342	0.6128	0.026*	
C9	1.1772 (2)	−0.3071 (2)	0.72177 (19)	0.0229 (4)	
H9	1.2640	−0.3650	0.7151	0.027*	
C10	1.0794 (2)	−0.3602 (2)	0.79243 (18)	0.0219 (4)	

C11	0.9534 (2)	−0.2700 (2)	0.79509 (17)	0.0185 (4)
H11	0.8843	−0.3047	0.8402	0.022*
C12	1.1083 (2)	−0.5075 (2)	0.8643 (2)	0.0299 (5)
H12A	1.1657	−0.5600	0.8175	0.045*
H12B	1.0255	−0.5299	0.8889	0.045*
H12C	1.1526	−0.5286	0.9334	0.045*
C13	0.70751 (19)	−0.0578 (2)	0.99095 (17)	0.0171 (4)
C14	0.7201 (2)	−0.0656 (2)	1.10211 (18)	0.0226 (4)
H14	0.6832	−0.1225	1.1692	0.027*
C15	0.7874 (2)	0.0109 (2)	1.11331 (18)	0.0232 (4)
H15	0.7978	0.0055	1.1887	0.028*
C16	0.8397 (2)	0.0957 (2)	1.01468 (18)	0.0191 (4)
C17	0.82251 (19)	0.0968 (2)	0.90710 (17)	0.0176 (4)
H17	0.8574	0.1539	0.8386	0.021*
C18	0.9108 (2)	0.1835 (2)	1.02124 (19)	0.0229 (4)
H18A	0.8465	0.2680	1.0244	0.034*
H18B	0.9721	0.2024	0.9520	0.034*
H18C	0.9601	0.1374	1.0916	0.034*
C19	0.63658 (19)	−0.13402 (19)	0.96885 (17)	0.0172 (4)
C20	0.5661 (2)	−0.2118 (2)	1.05512 (18)	0.0212 (4)
H20	0.5623	−0.2199	1.1341	0.025*
C21	0.5013 (2)	−0.2776 (2)	1.02487 (19)	0.0232 (4)
H21	0.4531	−0.3315	1.0833	0.028*
C22	0.5069 (2)	−0.2646 (2)	0.90901 (19)	0.0213 (4)
C23	0.57996 (19)	−0.1856 (2)	0.82881 (19)	0.0203 (4)
H23	0.5858	−0.1765	0.7494	0.024*
C24	0.4363 (2)	−0.3307 (2)	0.8704 (2)	0.0282 (5)
H24A	0.3629	−0.2622	0.8245	0.042*
H24B	0.4022	−0.3937	0.9390	0.042*
H24C	0.4979	−0.3795	0.8223	0.042*
C25	0.5617 (2)	0.1188 (2)	0.60673 (18)	0.0217 (4)
C26	0.4511 (3)	0.1848 (3)	0.5268 (3)	0.0453 (7)
H26A	0.4684	0.2620	0.4615	0.068*
H26B	0.3679	0.2152	0.5701	0.068*
H26C	0.4449	0.1203	0.4967	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01446 (13)	0.01728 (13)	0.01351 (13)	−0.00572 (10)	0.00119 (9)	−0.00706 (10)
Cl1	0.0257 (3)	0.0222 (2)	0.0203 (2)	−0.0080 (2)	0.00409 (19)	−0.00808 (19)
O1	0.0197 (7)	0.0241 (7)	0.0181 (7)	−0.0062 (6)	−0.0011 (5)	−0.0097 (6)
O2	0.0194 (7)	0.0261 (8)	0.0213 (7)	−0.0040 (6)	−0.0003 (6)	−0.0123 (6)
O3	0.0440 (10)	0.0332 (9)	0.0217 (8)	−0.0017 (8)	−0.0011 (7)	−0.0119 (7)
O4	0.0421 (11)	0.0382 (10)	0.0480 (11)	−0.0267 (9)	0.0166 (8)	−0.0230 (9)
O5	0.0352 (9)	0.0258 (8)	0.0244 (8)	−0.0097 (7)	0.0003 (7)	−0.0037 (7)
O6	0.0278 (9)	0.0414 (10)	0.0313 (9)	−0.0017 (8)	0.0034 (7)	−0.0164 (8)
O7A	0.0502 (19)	0.052 (2)	0.114 (3)	−0.005 (2)	−0.020 (2)	−0.023 (3)
O7B	0.0502 (19)	0.052 (2)	0.114 (3)	−0.005 (2)	−0.020 (2)	−0.023 (3)
N1	0.0191 (8)	0.0200 (8)	0.0139 (8)	−0.0081 (7)	0.0009 (6)	−0.0077 (6)
N2	0.0164 (8)	0.0209 (8)	0.0140 (7)	−0.0061 (7)	−0.0003 (6)	−0.0090 (6)

N3	0.0155 (8)	0.0173 (8)	0.0149 (8)	−0.0035 (6)	0.0002 (6)	−0.0071 (6)
N4	0.0148 (8)	0.0178 (8)	0.0177 (8)	−0.0055 (6)	0.0013 (6)	−0.0077 (6)
C1	0.0185 (9)	0.0248 (10)	0.0140 (9)	−0.0093 (8)	0.0012 (7)	−0.0101 (8)
C2	0.0202 (10)	0.0319 (11)	0.0212 (10)	−0.0140 (9)	0.0033 (8)	−0.0133 (9)
C3	0.0302 (11)	0.0311 (12)	0.0196 (10)	−0.0202 (10)	0.0047 (8)	−0.0112 (9)
C4	0.0334 (12)	0.0231 (10)	0.0160 (9)	−0.0150 (9)	0.0006 (8)	−0.0085 (8)
C5	0.0263 (11)	0.0199 (10)	0.0179 (9)	−0.0093 (8)	0.0036 (8)	−0.0093 (8)
C6	0.0421 (14)	0.0236 (11)	0.0250 (11)	−0.0159 (10)	0.0017 (10)	−0.0082 (9)
C7	0.0163 (9)	0.0243 (10)	0.0139 (9)	−0.0070 (8)	−0.0002 (7)	−0.0107 (8)
C8	0.0162 (10)	0.0320 (11)	0.0216 (10)	−0.0077 (8)	0.0014 (8)	−0.0156 (9)
C9	0.0164 (10)	0.0288 (11)	0.0254 (11)	−0.0004 (8)	−0.0040 (8)	−0.0163 (9)
C10	0.0237 (10)	0.0238 (10)	0.0198 (10)	−0.0019 (8)	−0.0066 (8)	−0.0118 (8)
C11	0.0205 (10)	0.0208 (10)	0.0152 (9)	−0.0057 (8)	−0.0010 (7)	−0.0083 (8)
C12	0.0324 (12)	0.0227 (11)	0.0282 (12)	0.0012 (9)	−0.0061 (9)	−0.0095 (9)
C13	0.0162 (9)	0.0164 (9)	0.0164 (9)	−0.0025 (7)	−0.0007 (7)	−0.0061 (7)
C14	0.0273 (11)	0.0231 (10)	0.0153 (9)	−0.0073 (9)	−0.0004 (8)	−0.0059 (8)
C15	0.0268 (11)	0.0248 (11)	0.0166 (9)	−0.0022 (9)	−0.0042 (8)	−0.0097 (8)
C16	0.0164 (9)	0.0196 (10)	0.0217 (10)	0.0002 (8)	−0.0043 (7)	−0.0113 (8)
C17	0.0160 (9)	0.0194 (9)	0.0183 (9)	−0.0044 (8)	−0.0001 (7)	−0.0091 (8)
C18	0.0228 (10)	0.0251 (11)	0.0254 (11)	−0.0044 (9)	−0.0052 (8)	−0.0146 (9)
C19	0.0147 (9)	0.0156 (9)	0.0181 (9)	−0.0018 (7)	0.0002 (7)	−0.0060 (7)
C20	0.0210 (10)	0.0183 (10)	0.0189 (10)	−0.0039 (8)	0.0019 (8)	−0.0045 (8)
C21	0.0195 (10)	0.0181 (10)	0.0266 (11)	−0.0064 (8)	0.0043 (8)	−0.0050 (8)
C22	0.0147 (9)	0.0184 (10)	0.0306 (11)	−0.0044 (8)	0.0010 (8)	−0.0104 (8)
C23	0.0152 (9)	0.0223 (10)	0.0279 (11)	−0.0068 (8)	0.0035 (8)	−0.0150 (9)
C24	0.0227 (11)	0.0275 (12)	0.0397 (13)	−0.0126 (9)	0.0026 (9)	−0.0155 (10)
C25	0.0211 (10)	0.0234 (10)	0.0208 (10)	−0.0060 (8)	−0.0027 (8)	−0.0083 (8)
C26	0.0394 (15)	0.0483 (16)	0.0450 (16)	0.0106 (13)	−0.0238 (12)	−0.0248 (13)

Geometric parameters (Å, º) for (1)

Ni1—N1	2.0510 (17)	C7—C8	1.392 (3)
Ni1—N4	2.0511 (17)	C8—C9	1.382 (3)
Ni1—N3	2.0706 (16)	C8—H8	0.9500
Ni1—N2	2.0784 (17)	C9—C10	1.390 (3)
Ni1—O1	2.1268 (14)	C9—H9	0.9500
Ni1—O2	2.1414 (15)	C10—C11	1.393 (3)
Cl1—O5	1.4346 (16)	C10—C12	1.505 (3)
Cl1—O6	1.4405 (17)	C11—H11	0.9500
Cl1—O4	1.4422 (18)	C12—H12A	0.9800
Cl1—O3	1.4437 (17)	C12—H12B	0.9800
O1—C25	1.266 (3)	C12—H12C	0.9800
O2—C25	1.271 (3)	C13—C14	1.393 (3)
O7A—O7B	0.871 (9)	C13—C19	1.481 (3)
O7A—H1W	0.885 (8)	C14—C15	1.385 (3)
O7A—H2W	0.886 (8)	C14—H14	0.9500
O7A—H3W	1.37 (8)	C15—C16	1.392 (3)
O7B—H1W	0.891 (10)	C15—H15	0.9500
O7B—H3W	0.886 (8)	C16—C17	1.394 (3)
N1—C5	1.337 (3)	C16—C18	1.504 (3)
N1—C1	1.350 (3)	C17—H17	0.9500

N2—C11	1.341 (3)	C18—H18A	0.9800
N2—C7	1.355 (3)	C18—H18B	0.9800
N3—C17	1.338 (3)	C18—H18C	0.9800
N3—C13	1.349 (3)	C19—C20	1.387 (3)
N4—C23	1.333 (3)	C20—C21	1.388 (3)
N4—C19	1.351 (3)	C20—H20	0.9500
C1—C2	1.390 (3)	C21—C22	1.390 (3)
C1—C7	1.478 (3)	C21—H21	0.9500
C2—C3	1.387 (3)	C22—C23	1.385 (3)
C2—H2	0.9500	C22—C24	1.502 (3)
C3—C4	1.391 (3)	C23—H23	0.9500
C3—H3	0.9500	C24—H24A	0.9800
C4—C5	1.390 (3)	C24—H24B	0.9800
C4—C6	1.501 (3)	C24—H24C	0.9800
C5—H5	0.9500	C25—C26	1.502 (3)
C6—H6A	0.9800	C26—H26A	0.9800
C6—H6B	0.9800	C26—H26B	0.9800
C6—H6C	0.9800	C26—H26C	0.9800
N1—Ni1—N4	174.56 (7)	C9—C8—H8	120.3
N1—Ni1—N3	96.73 (6)	C7—C8—H8	120.3
N4—Ni1—N3	79.38 (7)	C8—C9—C10	120.37 (19)
N1—Ni1—N2	79.39 (7)	C8—C9—H9	119.8
N4—Ni1—N2	97.14 (7)	C10—C9—H9	119.8
N3—Ni1—N2	95.96 (6)	C9—C10—C11	116.8 (2)
N1—Ni1—O1	91.24 (6)	C9—C10—C12	121.8 (2)
N4—Ni1—O1	93.59 (6)	C11—C10—C12	121.5 (2)
N3—Ni1—O1	161.67 (6)	N2—C11—C10	123.76 (19)
N2—Ni1—O1	101.73 (6)	N2—C11—H11	118.1
N1—Ni1—O2	94.43 (6)	C10—C11—H11	118.1
N4—Ni1—O2	90.06 (6)	C10—C12—H12A	109.5
N3—Ni1—O2	100.94 (6)	C10—C12—H12B	109.5
N2—Ni1—O2	162.60 (6)	H12A—C12—H12B	109.5
O1—Ni1—O2	61.87 (5)	C10—C12—H12C	109.5
O5—Cl1—O6	109.97 (11)	H12A—C12—H12C	109.5
O5—Cl1—O4	109.19 (12)	H12B—C12—H12C	109.5
O6—Cl1—O4	109.06 (11)	N3—C13—C14	121.31 (19)
O5—Cl1—O3	109.09 (10)	N3—C13—C19	115.18 (17)
O6—Cl1—O3	110.19 (11)	C14—C13—C19	123.52 (18)
O4—Cl1—O3	109.33 (11)	C15—C14—C13	119.02 (19)
C25—O1—Ni1	89.58 (12)	C15—C14—H14	120.5
C25—O2—Ni1	88.80 (12)	C13—C14—H14	120.5
O7B—O7A—H1W	61.0 (8)	C14—C15—C16	120.34 (19)
O7B—O7A—H2W	156 (3)	C14—C15—H15	119.8
H1W—O7A—H2W	98.5 (17)	C16—C15—H15	119.8
O7B—O7A—H3W	39 (4)	C15—C16—C17	116.69 (19)
H1W—O7A—H3W	69 (5)	C15—C16—C18	122.73 (18)
H2W—O7A—H3W	124 (6)	C17—C16—C18	120.57 (19)
O7A—O7B—H1W	60.3 (6)	N3—C17—C16	123.81 (19)
O7A—O7B—H3W	102 (9)	N3—C17—H17	118.1
H1W—O7B—H3W	97.8 (18)	C16—C17—H17	118.1

C5—N1—C1	119.03 (18)	C16—C18—H18A	109.5
C5—N1—Ni1	125.46 (14)	C16—C18—H18B	109.5
C1—N1—Ni1	115.50 (13)	H18A—C18—H18B	109.5
C11—N2—C7	118.74 (17)	C16—C18—H18C	109.5
C11—N2—Ni1	126.94 (14)	H18A—C18—H18C	109.5
C7—N2—Ni1	114.31 (13)	H18B—C18—H18C	109.5
C17—N3—C13	118.81 (17)	N4—C19—C20	120.95 (19)
C17—N3—Ni1	126.39 (13)	N4—C19—C13	115.20 (17)
C13—N3—Ni1	114.70 (13)	C20—C19—C13	123.84 (18)
C23—N4—C19	118.94 (17)	C19—C20—C21	119.31 (19)
C23—N4—Ni1	125.64 (14)	C19—C20—H20	120.3
C19—N4—Ni1	115.33 (13)	C21—C20—H20	120.3
N1—C1—C2	121.08 (19)	C20—C21—C22	119.93 (19)
N1—C1—C7	115.29 (17)	C20—C21—H21	120.0
C2—C1—C7	123.63 (19)	C22—C21—H21	120.0
C3—C2—C1	119.2 (2)	C23—C22—C21	116.87 (19)
C3—C2—H2	120.4	C23—C22—C24	120.7 (2)
C1—C2—H2	120.4	C21—C22—C24	122.5 (2)
C2—C3—C4	120.20 (19)	N4—C23—C22	124.0 (2)
C2—C3—H3	119.9	N4—C23—H23	118.0
C4—C3—H3	119.9	C22—C23—H23	118.0
C5—C4—C3	116.8 (2)	C22—C24—H24A	109.5
C5—C4—C6	120.6 (2)	C22—C24—H24B	109.5
C3—C4—C6	122.6 (2)	H24A—C24—H24B	109.5
N1—C5—C4	123.7 (2)	C22—C24—H24C	109.5
N1—C5—H5	118.2	H24A—C24—H24C	109.5
C4—C5—H5	118.2	H24B—C24—H24C	109.5
C4—C6—H6A	109.5	O1—C25—O2	119.72 (19)
C4—C6—H6B	109.5	O1—C25—C26	120.2 (2)
H6A—C6—H6B	109.5	O2—C25—C26	120.1 (2)
C4—C6—H6C	109.5	C25—C26—H26A	109.5
H6A—C6—H6C	109.5	C25—C26—H26B	109.5
H6B—C6—H6C	109.5	H26A—C26—H26B	109.5
N2—C7—C8	121.00 (19)	C25—C26—H26C	109.5
N2—C7—C1	115.49 (17)	H26A—C26—H26C	109.5
C8—C7—C1	123.51 (18)	H26B—C26—H26C	109.5
C9—C8—C7	119.3 (2)		
C5—N1—C1—C2	0.5 (3)	C17—N3—C13—C19	178.34 (17)
Ni1—N1—C1—C2	179.49 (15)	Ni1—N3—C13—C19	−5.0 (2)
C5—N1—C1—C7	−179.44 (17)	N3—C13—C14—C15	0.2 (3)
Ni1—N1—C1—C7	−0.5 (2)	C19—C13—C14—C15	−179.34 (19)
N1—C1—C2—C3	−0.3 (3)	C13—C14—C15—C16	1.0 (3)
C7—C1—C2—C3	179.70 (18)	C14—C15—C16—C17	−1.0 (3)
C1—C2—C3—C4	−0.4 (3)	C14—C15—C16—C18	178.50 (19)
C2—C3—C4—C5	0.8 (3)	C13—N3—C17—C16	1.2 (3)
C2—C3—C4—C6	−178.3 (2)	Ni1—N3—C17—C16	−175.11 (15)
C1—N1—C5—C4	−0.1 (3)	C15—C16—C17—N3	0.0 (3)
Ni1—N1—C5—C4	−178.94 (15)	C18—C16—C17—N3	−179.57 (18)
C3—C4—C5—N1	−0.6 (3)	C23—N4—C19—C20	−0.3 (3)
C6—C4—C5—N1	178.56 (19)	Ni1—N4—C19—C20	176.39 (15)

C11—N2—C7—C8	1.5 (3)	C23—N4—C19—C13	−179.20 (17)
Ni1—N2—C7—C8	−179.70 (14)	Ni1—N4—C19—C13	−2.5 (2)
C11—N2—C7—C1	−178.06 (16)	N3—C13—C19—N4	5.0 (3)
Ni1—N2—C7—C1	0.7 (2)	C14—C13—C19—N4	−175.41 (18)
N1—C1—C7—N2	−0.1 (2)	N3—C13—C19—C20	−173.90 (18)
C2—C1—C7—N2	179.88 (18)	C14—C13—C19—C20	5.7 (3)
N1—C1—C7—C8	−179.73 (18)	N4—C19—C20—C21	0.1 (3)
C2—C1—C7—C8	0.3 (3)	C13—C19—C20—C21	178.98 (19)
N2—C7—C8—C9	−2.0 (3)	C19—C20—C21—C22	−0.3 (3)
C1—C7—C8—C9	177.59 (18)	C20—C21—C22—C23	0.6 (3)
C7—C8—C9—C10	0.1 (3)	C20—C21—C22—C24	−178.6 (2)
C8—C9—C10—C11	2.1 (3)	C19—N4—C23—C22	0.6 (3)
C8—C9—C10—C12	−176.87 (19)	Ni1—N4—C23—C22	−175.66 (15)
C7—N2—C11—C10	0.8 (3)	C21—C22—C23—N4	−0.8 (3)
Ni1—N2—C11—C10	−177.76 (14)	C24—C22—C23—N4	178.44 (19)
C9—C10—C11—N2	−2.6 (3)	Ni1—O1—C25—O2	1.4 (2)
C12—C10—C11—N2	176.34 (19)	Ni1—O1—C25—C26	−178.7 (2)
C17—N3—C13—C14	−1.3 (3)	Ni1—O2—C25—O1	−1.3 (2)
Ni1—N3—C13—C14	175.44 (15)	Ni1—O2—C25—C26	178.7 (2)

Hydrogen-bond geometry (Å, º) for (1)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O7A—H1W⋯O4	0.89 (1)	2.19 (1)	2.971 (5)	147 (2)
O7B—H1W⋯O4	0.89 (1)	2.19 (1)	3.011 (10)	153 (2)
O7A—H2W⋯O2	0.89 (1)	2.13 (1)	2.974 (5)	159 (3)
O7B—H3W⋯O7A[i]	0.89 (1)	2.33 (5)	3.144 (12)	152 (11)
O7B—H3W⋯O7B[i]	0.89 (1)	2.46 (10)	3.19 (2)	140 (12)
C2—H2⋯O1[ii]	0.95	2.52	3.376 (3)	151
C3—H3⋯O5[iii]	0.95	2.37	3.285 (3)	161
C5—H5⋯O2	0.95	2.64	3.198 (3)	118
C20—H20⋯O2[iv]	0.95	2.56	3.421 (3)	152
C21—H21⋯O4[iv]	0.95	2.33	3.267 (3)	169
C23—H23⋯O1	0.95	2.60	3.158 (3)	118
C23—H23⋯O5[v]	0.95	2.60	3.187 (3)	120
C26—H26A⋯O7B[i]	0.98	2.44	3.334 (11)	151

Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x+2, −y, −z+1; (iii) −x+2, −y+1, −z+1; (iv) −x+1, −y, −z+2; (v) x, y−1, z.