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Crystal structure of a zigzag Co^{II} coordination polymer: *catena*-poly[[dichloridobis(methanol-κO)cobalt(II)]-μ-bis(pyridin-3-ylmethyl)sulfane-$\kappa^2 N$:N']

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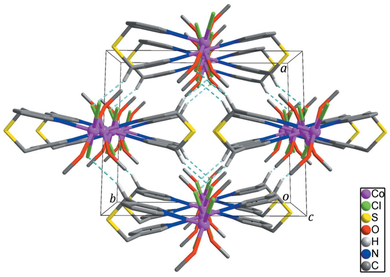
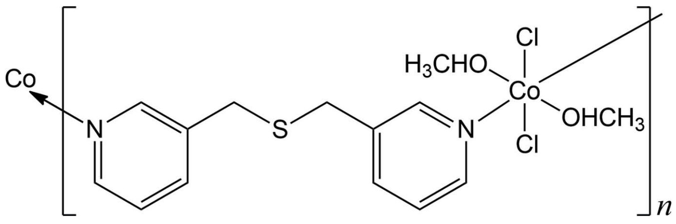
Reaction of bis(pyridin-3-ylmethyl)sulfane (*L*) with cobalt(II) chloride in methanol led to the formation of the title coordination polymer, $[CoCl_2(C_{12}H_{12}N_2S)(CH_3OH)_2]_n$, in which the Co^{II} cation lies on a crystallographic inversion centre and the S atom of the *L* ligand lies on a twofold rotation axis. Each Co^{II} ion is coordinated by two pyridine N atoms from two bridging *L* ligands, two O atoms from methanol molecules and two chloride anions, all inversion-related. The complex unit has an elongated octahedral geometry, in which N_2O_2 donor atoms occupy the equatorial positions and two chloride anions occupy the axial positions. Each *L* ligand links two Co^{II} ions, forming an infinite zigzag chain propagating along the *c*-axis direction and further stabilized by O—H⋯Cl hydrogen bonds between the methanol molecules and the chloride anions. Adjacent chains in the structure are connected by intermolecular C—H⋯Cl hydrogen bonds, resulting in the formation of a three-dimensional supramolecular architecture.



1. Chemical context

Up to now, large numbers of metal–organic coordination polymers with intriguing topologies and attractive properties have been constructed in which dipyridyl-type molecules functioning as bridging ligands have mainly been used (Leong & Vittal, 2011; Wang *et al.*, 2012; Liu *et al.*, 2011). Our group has also investigated several metal–organic coordination polymers with interesting topologies using such dipyridyl-type ligands (Moon *et al.*, 2011, 2016, 2017; Lee *et al.*, 2015; Ju *et al.*, 2014; Im *et al.*, 2017). In an extension of our research in this area, the title compound was prepared by the reaction of cobalt(II) chloride with bis(pyridin-3-ylmethyl)sulfane, $C_{12}H_{12}N_2S$, (*L*) as a flexible dipyridyl-type ligand [synthesized according to a literature procedure (Park *et al.*, 2010; Lee *et al.*, 2012)]. Our group has previously reported the crystal structure of a looped-chain Co^{II} coordination polymer obtained through the reaction of cobalt(II) nitrate with *L* (Moon *et al.*, 2017). In this article, we describe the crystal structure of the title compound, $[Co(L)(CH_3OH)_2Cl_2]_n$, with *L* = (pyridin-3-ylmethyl)sulfane, which adopts a one-dimensional zigzag topology.



2. Structural commentary

As shown in Figs. 1 and 2, the molecular structure of the title compound is generated by the combination of inversion and twofold rotation symmetries. Each Co^{II} cation lies on a crystallographic inversion centre, and the twofold rotation axis passes through the S atom of the *L* ligand. Therefore, the asymmetric unit comprises one half of a Co^{II} cation, one half of an *L* ligand, one chloride anion and one methanol molecule. The coordination geometry of the Co^{II} ion is elongated octahedral with the four equatorial positions being occupied by two pyridine N atoms from the two symmetry-related *L* ligands and two O atoms from two symmetry-related methanol molecules, and the two axial positions being occupied by two chlorido ligands (Fig. 1). Selected bond lengths and angles around the Co1 atom are listed in Table 1. The coordination geometry of the title compound is similar to that found in dichlorobis(methanol-*κO*)bis[*N*-(1-naphthyl)-*N*′-(3-pyridyl)urea-*κN*]cobalt(II) (Huang *et al.*, 2008).

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.119 (2)	Co1—Cl1	2.4571 (11)
Co1—N1	2.153 (3)		
O1—Co1—N1	88.20 (11)	N1—Co1—Cl1	92.11 (9)
O1—Co1—Cl1	90.53 (8)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*A*⋯Cl1^{i}	0.82	2.28	3.030 (3)	152
C6—H6*A*⋯Cl1^{ii}	0.97	2.76	3.653 (4)	153

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

Each *L* ligand bridges two Co^{II} ions into an infinite zigzag chain propagating along the *c*-axis direction (Fig. 2). The separation between the Co^{II} ions through a *L* ligand in the chain is 6.0595 (11) Å. The flexible thioether segment [C5—C6—S1—C6^{iv}—C5^{iv}; symmetry code: (iv) $-x+1, y, -z-\frac{1}{2}$] of the *L* ligand shows a bent arrangement induced by a *gauche*–*gauche* configuration with a torsion angle of 74.4 (3)° for the C5—C6—S1—C6^{iv} and C6—S1—C6^{iv}—C5^{iv} units. This conformation of the *L* ligand is similar to those in a cyclic dimer-type silver(I) BF_4 complex, $[Ag(L)]_2{\cdot}2BF_4$ (Seo *et al.*, 2003), and a staircase-type copper(I) iodide coordination polymer, $[(CuI)_2(L)]_n$ (Hanton *et al.*, 2006). The zigzag topology of the chain may be induced by this conformation of the *L* ligand.

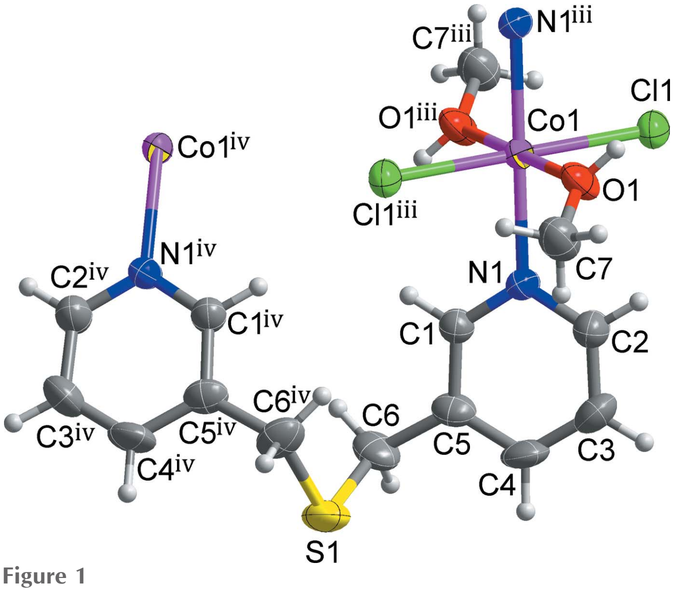


Figure 1
A view of molecular structure of the title compound, showing the geometry around the Co^{II} centre and the atom-numbering scheme [symmetry codes: (iii) $-x+1, -y, -z$; (iv) $-x+1, y, -z-\frac{1}{2}$]. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

3. Supramolecular features

An O1—H⋯Cl1^{i} hydrogen bond (Table 2; yellow dashed lines in Fig. 2; symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$) between the methanol molecule and the chloride anion contributes to the stabilization of the zigzag chain. In the crystal, weak C6—H⋯Cl1^{ii} hydrogen bonds (Table 2; sky-blue dashed lines in Fig. 3) connect neighboring zigzag chains to generate a three-dimensional supramolecular network.

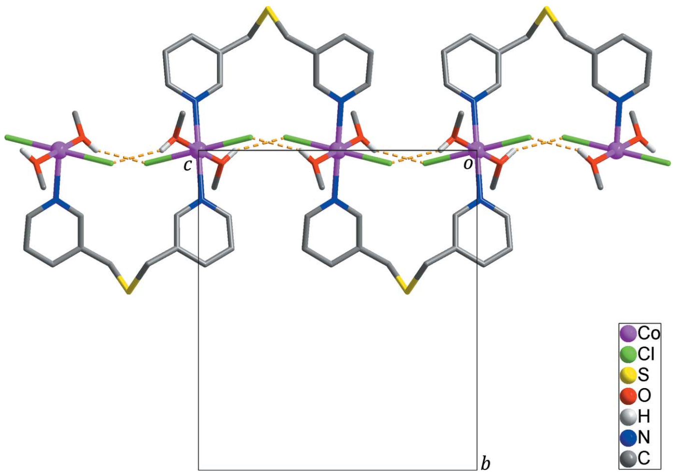


Figure 2
The zigzag chain structure of the title compound extending along the *c* axis. Yellow dashed lines represent intramolecular O—H⋯Cl hydrogen bonds in the zigzag chain. H atoms not involved in intermolecular interactions have been omitted for clarity.

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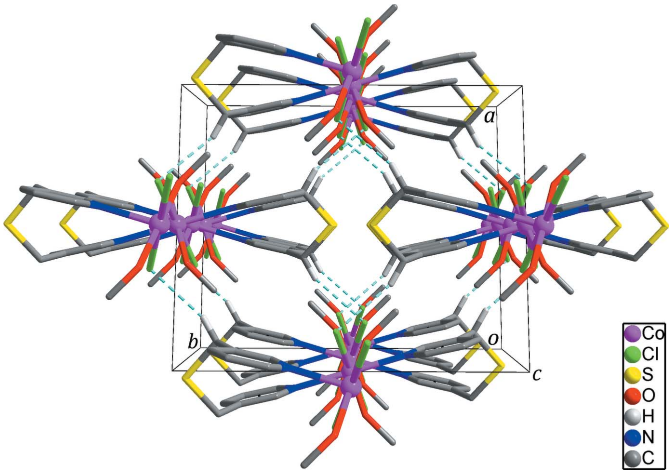

Figure 3
The three-dimensional supramolecular network formed through intermolecular C—H⋯Cl hydrogen bonds (sky-blue dashed lines) between the chains. H atoms not involved in intermolecular interactions have been omitted for clarity.

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) for the title ligand (*L*) gave three hits. Two of these (REJCAL, RENHOI; Hanton *et al.*, 2006) are copper(I) iodide coordination polymers adopting staircase- and loop-type structures, respectively. The third (EXEZOW; Seo *et al.*, 2003) is a silver(I) BF_4 complex with a cyclic dimer structure.

5. Synthesis and crystallization

The *L* ligand was synthesized according to a literature method (Park *et al.*, 2010; Lee *et al.*, 2012). Crystals of the title compound were obtained by slow evaporation of a methanol solution of the *L* ligand with $CoCl_2·6H_2O$ in an 1:1 molar ratio.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were positioned geometrically with C—H = 0.93 Å for C*sp*^{2}—H, 0.96 Å for methyl C—H, 0.97 Å for methylene C—H, and 0.82 Å for alcohol O—H, and were refined as riding with U_{iso}(H) = 1.2U_{eq}(C,O).

Table 3
Experimental details.

Crystal data	
Chemical formula	$[CoCl_2(C_{12}H_{12}N_2S)(CH_4O)_2]$
M_r	410.21
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	298
a, *b*, *c* (Å)	11.419 (2), 13.363 (2), 12.119 (2)
β (°)	106.226 (4)
V (Å^3)	1775.6 (6)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.39
Crystal size (mm)	0.35 × 0.08 × 0.08
Data collection	
Diffractometer	Bruker CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.627, 0.888
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5461, 1947, 1013
R_{int}	0.098
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.095, 0.92
No. of reflections	1947
No. of parameters	102
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.32

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2010) and *publCIF* (Westrip, 2010).

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supporting information

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Crystal structure of a zigzag Co^{II} coordination polymer: *catena*-poly[[dichloridobis(methanol-*κO*)cobalt(II)]-*μ*-bis(pyridin-3-ylmethyl)sulfane-*κ*^{2}*N*:*N′*]

Suk-Hee Moon, Joobeom Seo and Ki-Min Park

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

catena-Poly[[dichloridobis(methanol-*κO*)cobalt(II)]-*μ*-bis(pyridin-3-ylmethyl)sulfane-*κ*^{2}*N*:*N′*]

Crystal data

$[CoCl_2(C_{12}H_{12}N_2S)(CH_4O)_2]$
M_r = 410.21
Monoclinic, $C2/c$
a = 11.419 (2) Å
b = 13.363 (2) Å
c = 12.119 (2) Å
β = 106.226 (4)°
V = 1775.6 (6) Å^3
Z = 4
$F(000)$ = 844
D_x = 1.534 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5771 reflections
θ = 2.4–28.2°
μ = 1.39 mm^{-1}
T = 298 K
Needle, violet
0.35 × 0.08 × 0.08 mm

Data collection

Bruker CCD area detector diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.627, T_{max} = 0.888
5461 measured reflections
1947 independent reflections
1013 reflections with $I > 2\sigma(I)$
R_{int} = 0.098
θ_{max} = 27.0°, θ_{min} = 2.4°
$h = -14 \rightarrow 14$
$k = -17 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.095
S = 0.92
1947 reflections
102 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.0000	0.0000	0.0333 (2)
Cl1	0.64563 (9)	0.04038 (8)	0.18588 (8)	0.0414 (3)
S1	0.5000	−0.44202 (11)	−0.2500	0.0611 (5)
O1	0.3665 (2)	−0.0394 (2)	0.0836 (2)	0.0467 (8)
H1A	0.3528	−0.0010	0.1313	0.056*
N1	0.5559 (3)	−0.1544 (2)	0.0120 (3)	0.0361 (8)
C1	0.5742 (3)	−0.2051 (3)	−0.0774 (3)	0.0365 (10)
H1	0.5682	−0.1696	−0.1448	0.044*
C2	0.5680 (4)	−0.2068 (3)	0.1089 (4)	0.0467 (12)
H2	0.5578	−0.1734	0.1729	0.056*
C3	0.5946 (4)	−0.3071 (4)	0.1189 (4)	0.0599 (14)
H3	0.6021	−0.3408	0.1877	0.072*
C4	0.6099 (4)	−0.3567 (3)	0.0235 (4)	0.0562 (13)
H4	0.6262	−0.4250	0.0274	0.067*
C5	0.6011 (4)	−0.3051 (3)	−0.0771 (4)	0.0416 (11)
C6	0.6204 (4)	−0.3550 (3)	−0.1819 (4)	0.0543 (13)
H6A	0.6975	−0.3907	−0.1601	0.065*
H6B	0.6260	−0.3040	−0.2372	0.065*
C7	0.2751 (4)	−0.1150 (3)	0.0567 (4)	0.0570 (13)
H7A	0.2241	−0.1053	−0.0202	0.068*
H7B	0.2265	−0.1112	0.1096	0.068*
H7C	0.3132	−0.1796	0.0625	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0461 (5)	0.0281 (5)	0.0281 (4)	0.0030 (4)	0.0143 (4)	0.0000 (4)
Cl1	0.0512 (7)	0.0429 (6)	0.0305 (6)	0.0051 (5)	0.0122 (5)	0.0002 (4)
S1	0.0791 (14)	0.0273 (10)	0.0658 (13)	0.000	0.0021 (11)	0.000
O1	0.064 (2)	0.0387 (17)	0.0454 (18)	−0.0111 (15)	0.0286 (17)	−0.0149 (13)
N1	0.048 (2)	0.029 (2)	0.034 (2)	0.0012 (16)	0.0140 (18)	0.0029 (16)
C1	0.039 (3)	0.035 (3)	0.035 (2)	0.004 (2)	0.010 (2)	0.000 (2)
C2	0.061 (3)	0.041 (3)	0.039 (3)	0.006 (2)	0.016 (2)	0.002 (2)
C3	0.080 (4)	0.047 (3)	0.050 (3)	0.005 (3)	0.013 (3)	0.020 (3)
C4	0.072 (4)	0.025 (3)	0.067 (4)	0.010 (2)	0.012 (3)	0.010 (2)
C5	0.034 (3)	0.033 (3)	0.056 (3)	0.006 (2)	0.011 (2)	−0.003 (2)
C6	0.052 (3)	0.045 (3)	0.064 (3)	0.015 (2)	0.015 (3)	−0.014 (2)
C7	0.068 (3)	0.054 (3)	0.052 (3)	−0.013 (3)	0.022 (3)	−0.008 (2)

Geometric parameters (Å, º)

Co1—O1	2.119 (2)	C1—H1	0.9300
Co1—O1^{i}	2.119 (2)	C2—C3	1.372 (6)
Co1—N1	2.153 (3)	C2—H2	0.9300
Co1—N1^{i}	2.153 (3)	C3—C4	1.385 (6)
Co1—Cl1^{i}	2.4571 (11)	C3—H3	0.9300
Co1—Cl1	2.4571 (11)	C4—C5	1.380 (6)
S1—C6	1.814 (4)	C4—H4	0.9300
S1—C6^{ii}	1.814 (4)	C5—C6	1.504 (5)
O1—C7	1.424 (4)	C6—H6A	0.9700
O1—H1A	0.8200	C6—H6B	0.9700
N1—C2	1.342 (5)	C7—H7A	0.9600
N1—C1	1.343 (5)	C7—H7B	0.9600
C1—C5	1.371 (5)	C7—H7C	0.9600

O1—Co1—O1^{i}	180.0	N1—C2—C3	123.6 (4)
O1—Co1—N1	88.20 (11)	N1—C2—H2	118.2
O1^{i}—Co1—N1	91.80 (11)	C3—C2—H2	118.2
O1—Co1—N1^{i}	91.80 (11)	C2—C3—C4	118.0 (4)
O1^{i}—Co1—N1^{i}	88.20 (11)	C2—C3—H3	121.0
N1—Co1—N1^{i}	180.0	C4—C3—H3	121.0
O1—Co1—Cl1^{i}	89.47 (8)	C5—C4—C3	120.3 (4)
O1^{i}—Co1—Cl1^{i}	90.53 (8)	C5—C4—H4	119.9
N1—Co1—Cl1^{i}	87.89 (9)	C3—C4—H4	119.9
N1^{i}—Co1—Cl1^{i}	92.11 (9)	C1—C5—C4	116.7 (4)
O1—Co1—Cl1	90.53 (8)	C1—C5—C6	121.0 (4)
O1^{i}—Co1—Cl1	89.47 (8)	C4—C5—C6	122.2 (4)
N1—Co1—Cl1	92.11 (9)	C5—C6—S1	113.4 (3)
N1^{i}—Co1—Cl1	87.89 (9)	C5—C6—H6A	108.9
Cl1^{i}—Co1—Cl1	180.0	S1—C6—H6A	108.9
C6—S1—C6^{ii}	100.3 (3)	C5—C6—H6B	108.9
C7—O1—Co1	130.2 (2)	S1—C6—H6B	108.9
C7—O1—H1A	109.5	H6A—C6—H6B	107.7
Co1—O1—H1A	119.1	O1—C7—H7A	109.5
C2—N1—C1	116.2 (4)	O1—C7—H7B	109.5
C2—N1—Co1	121.1 (3)	H7A—C7—H7B	109.5
C1—N1—Co1	122.6 (3)	O1—C7—H7C	109.5
N1—C1—C5	125.1 (4)	H7A—C7—H7C	109.5
N1—C1—H1	117.5	H7B—C7—H7C	109.5
C5—C1—H1	117.5		

C2—N1—C1—C5	1.6 (6)	N1—C1—C5—C6	−179.8 (4)
Co1—N1—C1—C5	−175.0 (3)	C3—C4—C5—C1	−1.4 (7)
C1—N1—C2—C3	−1.6 (6)	C3—C4—C5—C6	178.3 (4)
Co1—N1—C2—C3	175.1 (3)	C1—C5—C6—S1	−110.7 (4)
N1—C2—C3—C4	0.1 (7)	C4—C5—C6—S1	69.6 (5)

C2—C3—C4—C5	1.4 (7)	C6^{ii}—S1—C6—C5	74.4 (3)
N1—C1—C5—C4	−0.1 (6)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Cl1^{iii}	0.82	2.28	3.030 (3)	152
C6—H6*A*···Cl1^{iv}	0.97	2.76	3.653 (4)	153

Symmetry codes: (iii) −*x*+1, *y*, −*z*+1/2; (iv) −*x*+3/2, −*y*−1/2, −*z*.