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Nickel(II) uranium(IV) trisulfide

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Key indicators: single-crystal X-ray study; T = 100 K; mean σ(U–S) = 0.001 Å; R factor = 0.018; wR factor = 0.043; data-to-parameter ratio = 25.8.

Crystals of $NiUS_3$ were obtained from the reaction of the elements Ni, U, S, and of GeI_2 in a CsCl flux at 1173 K. Nickel(II) uranium(IV) trisulfide, $NiUS_3$, has orthorhombic (*Pnma*) symmetry and crystallizes in the $GdFeO_3$ structure type. The compound has a perovskite ABQ_3-like structure, with U occupying the interstitial sites of a NiS_6 framework. The U atoms are coordinated by eight S atoms in a distorted bicapped trigonal–prismatic arrangement. The Ni atoms are coordinated by six S atoms in a slightly distorted octahedral arrangement. The asymmetric unit comprises one U site (site symmetry *.m.*), one Ni site ($\bar{1}$), and two S sites (1 and *.m.*).

Related literature

Uranium chalcogenides of the composition ABQ_3 are known for Sc, V–Ni, Pd, Ru, Rh, and Ba (for a review, see: Narducci & Ibers, 1998). These compounds all have perovskite-type structures with A atoms occupying eight-coordinate interstitial sites within a BQ_6 framework. There are two subclasses of the ABQ_3 structure, *viz*. $GdFeO_3$ (*Pnma)* (Marezio *et al.*, 1970) and $FeUS_3$ (*Cmcm)* (Noël & Padiou, 1976). Single-crystal refinements have been carried out for $BaUS_3$ (Brochu *et al.*, 1970), $CrUS_3$ (Noël *et al.*, 1975), $FeUQ_3$ (Q = S, Se) (Noël & Padiou, 1976; Jin *et al.*, 2010), $ScUS_3$ (Julien *et al.*, 1978), $RhUS_3$ (Daoudi & Noël, 1987), $PdUSe_3$ (Daoudi & Noël, 1989), and $MnUSe_3$ (Ijjaali *et al.*, 2004). The unit cell of $NiUS_3$ was determined previously from powder diffracton experiments (Noël *et al.*, 1971). For standardization of structural data, see: Gelato & Parthé (1987).

Experimental

Crystal data

$NiUS_3$
M_r = 392.92
Orthorhombic, *Pnma*
a = 6.8924 (3) Å
b = 8.7570 (4) Å
c = 6.0758 (2) Å
V = 366.72 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 50.68 mm^{-1}
T = 100 K
0.09 × 0.09 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: numerical (*SADABS*; Bruker, 2009)
T_{min} = 0.093, T_{max} = 0.108
7334 measured reflections
748 independent reflections
728 reflections with $I > 2\sigma(I)$
R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.043
S = 1.36
748 reflections
29 parameters
$\Delta\rho_{max}$ = 2.80 e Å^{-3}
$\Delta\rho_{min}$ = −1.15 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2013); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: *CrystalMaker* (Palmer, 2009); software used to prepare material for publication: *SHELXL2013*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2789).

References

Brochu, R., Padiou, J. & Grandjean, D. (1970). *C. R. Seances Acad. Sci. Ser. C*, **271**, 642–643.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Daoudi, A. & Noël, H. (1987). *Inorg. Chim. Acta*, **140**, 93–95.
Daoudi, A. & Noël, H. (1989). *J. Less Common Met.* **153**, 293–298.
Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.
Ijjaali, I., Mitchell, K., Huang, F. Q. & Ibers, J. A. (2004). *J. Solid State Chem.* **177**, 257–261.
Jin, G. B., Ringe, E., Long, G. J., Grandjean, F., Sougrati, M. T., Choi, E. S., Wells, D. M., Balasubramanian, M. & Ibers, J. A. (2010). *Inorg. Chem.* **49**, 10455–10467.
Julien, R., Rodier, N. & Tien, V. (1978). *Acta Cryst.* B**34**, 2612–2614.
Marezio, M., Remeika, J. P. & Dernier, P. D. (1970). *Acta Cryst.* B**26**, 2008–2022.
Narducci, A. A. & Ibers, J. A. (1998). *Chem. Mater.* **10**, 2811–2823.
Noël, H. & Padiou, J. (1976). *Acta Cryst.* B**32**, 1593–1595.
Noël, H., Padiou, J. & Prigent, J. (1971). *C. R. Seances Acad. Sci. Ser. C*, **272**, 206–208.
Noël, H., Padiou, J. & Prigent, J. (1975). *C. R. Seances Acad. Sci. Ser. C*, **280**, 123–126.
Palmer, D. (2009). *CrystalMaker*. CrystalMaker Software Ltd, Yarnton, Oxfordshire, England.
Sheldrick, G. M. (2013). *SHELX2013*. University of Göttingen, Germany.

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S1. Comment

$NiUS_3$ crystallizes in the orthorhombic space group *Pnma*. Its unit cell was previously determined (Noël *et al.*, 1971), revealing the compound to be isostructral with uranium compounds with analogous compositions. A number of uranium chalcogenides of the composition ABQ_3 are known (for a review, see: Narducci & Ibers, 1998) and crystallize in two subclasses, *viz*. $GdFeO_3$ (*Pnma*) (Marezio *et al.*, 1970) and $FeUS_3$ (*Cmcm*) (Noël & Padiou, 1976). Most of the ABQ_3 compounds crystallize in the three-dimesional $GdFeO_3$ structure type. However, when *B* = Sc, Fe, or Mn, they crystallize in the layered $FeUS_3$ structure type. Refinements based on single crystal data have been carried out for $BaUS_3$ (Brochu *et al.*, 1970), $CrUS_3$ (Noël *et al.*, 1975), $FeUQ_3$ (*Q* = S, Se) (Noël & Padiou, 1976; Jin *et al.*, 2010), $ScUS_3$ (Julien *et al.*, 1978), $RhUS_3$ (Daoudi & Noël, 1987), $PdUSe_3$ (Daoudi & Noël, 1989), and $MnUSe_3$ (Ijjaali *et al.*, 2004).

The structure is composed of one U site, one Ni site, and two S sites. The uranium atoms are coordinated by eight S atoms in a distorted bicapped trigonal-prismatic arrangement. The Ni atoms are coordinated by six S atoms in a slightly distorted octahedral arrangement. The unit cell is shown in Figure 1 and a packing diagram is shown in Figure 2. There is no evidence of S—S bonding and thus formal oxidation states may be assigned as +II,+IV, and –II for Ni, U, and S, respectively. U—S distances range from 2.6666 (13) Å to 3.0088 (8) Å. These distances compare favorably with the U—S distances in the related compound $RhUS_3$ (Daoudi & Noël, 1987). Ni—S distances range from 2.3386 (4) Å to 2.4739 (9) Å.

S2. Experimental

$NiUS_3$ was obtained from the reaction of U (0.126 mmol), GeI_2 (0.063 mmol), Ni (0.126 mmol), and S (0.378 mmol) in a CsCl flux (0.445 mmol). The reactants were loaded into a carbon-coated fused-silica tube under an inert Ar atmosphere that was evacuated to 10^{-4} Torr. The tube was then flame sealed. It was placed in a computer-controlled furnace and heated to 1173 K in 12 h, held there for 6 h, cooled to 1073 K in 12 h and then held there for a further 96 h. The tube was next cooled at 5 K/h to 773 K and then to 298 K in 12 h. The reaction yielded black prisms of $NiUS_3$ and black rectangular plates of NiU_8S_{17} (Noël *et al.*, 1971). The crystals were washed with water and dried with acetone to remove excess flux. They are stable to both air and moisture.

S3. Refinement

Atomic positions were standardized with the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The highest peak of 2.8 (3) $e^-/Å^3$ is 1.81 Å from atom S2 and the deepest hole of -1.2 (3) $e^-/Å^3$ is 0.96 Å from atom U1.

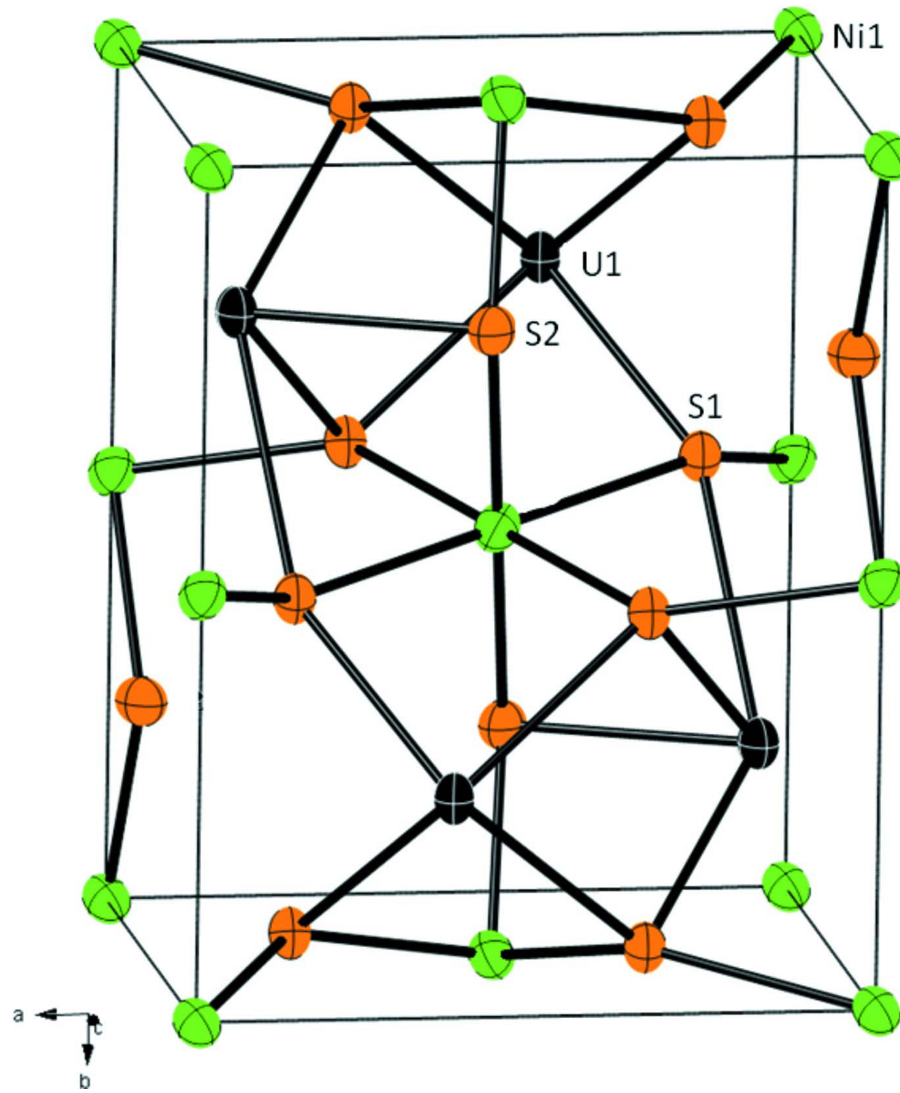

Figure 1

The unit cell of $NiUS_3$. Displacement ellipsoids at the 95% probability level are shown.

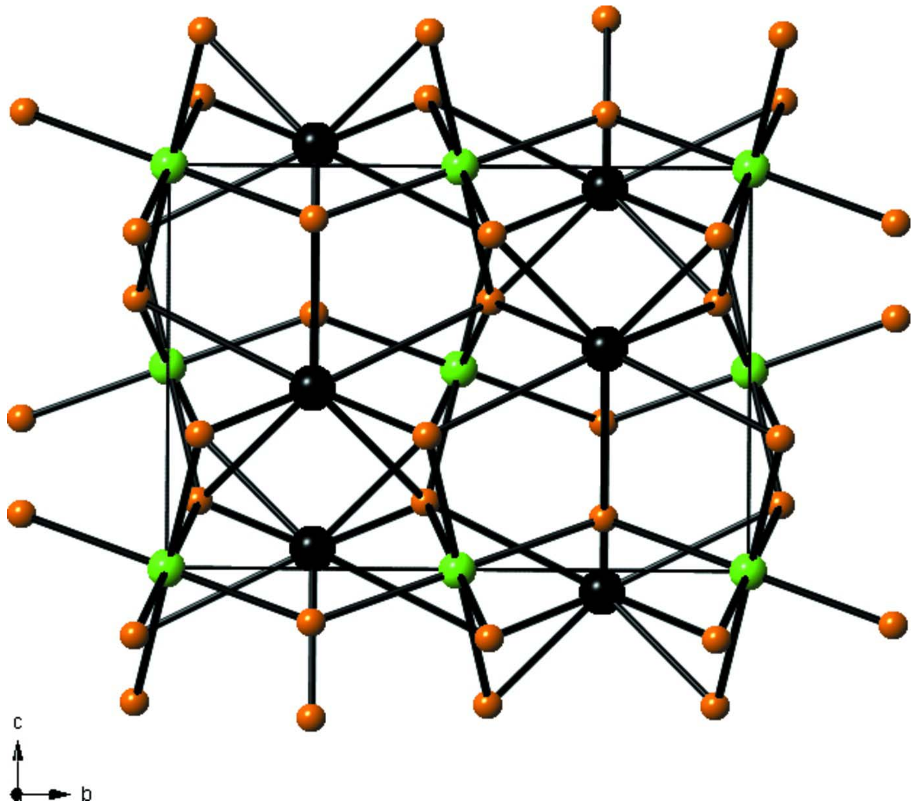

Figure 2

A packing diagram of $NiUS_3$ viewed down the *a* axis. Ni atoms are green, U atoms are black, and S atoms are orange.

Nickel(II) uranium(IV) trisulfide

Crystal data

$NiUS_3$
M_r = 392.92
Orthorhombic, *Pnma*
a = 6.8924 (3) Å
b = 8.7570 (4) Å
c = 6.0758 (2) Å
V = 366.72 (3) $Å^3$
Z = 4
F(000) = 672
D_x = 7.117 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3973 reflections
θ = 4.1–33.2°
μ = 50.68 mm^{-1}
T = 100 K
Prism, black
0.09 × 0.09 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
φ and *ω* scans
Absorption correction: numerical (*SADABS*; Bruker, 2009)
T_{min} = 0.093, T_{max} = 0.108
7334 measured reflections
748 independent reflections
728 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 33.2°, θ_{min} = 4.1°
h = −10→10
k = −13→13
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.043$
$S = 1.36$
748 reflections
29 parameters
0 restraints

$w = 1/[\sigma^2(F_o^2) + (0.0149F_o^2)^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.80$ e Å^{-3}
$\Delta\rho_{min} = -1.15$ e Å^{-3}
Extinction correction: *SHELXL2013* (Sheldrick, 2013), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0039 (4)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
U1	0.38141 (3)	0.2500	0.05064 (3)	0.00770 (8)
Ni1	0.0000	0.0000	0.0000	0.00778 (13)
S1	0.18039 (14)	0.05448 (9)	0.33217 (13)	0.00731 (15)
S2	0.52930 (19)	0.2500	0.63121 (19)	0.0085 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.00525 (11)	0.00896 (10)	0.00890 (10)	0.000	0.00069 (5)	0.000
Ni1	0.0069 (3)	0.0081 (2)	0.0083 (2)	−0.0009 (2)	−0.0008 (2)	0.0002 (2)
S1	0.0057 (4)	0.0087 (3)	0.0075 (3)	0.0000 (3)	0.0000 (3)	0.0004 (3)
S2	0.0081 (6)	0.0079 (4)	0.0095 (5)	0.000	0.0023 (4)	0.000

Geometric parameters (Å, º)

U1—S2^{i}	2.6666 (13)	Ni1—S1^{ix}	2.4180 (8)
U1—S2^{ii}	2.7446 (12)	Ni1—S1	2.4180 (8)
U1—S1^{iii}	2.7721 (9)	Ni1—S1^{i}	2.4739 (9)
U1—S1^{iv}	2.7721 (9)	Ni1—S1^{vi}	2.4739 (9)
U1—S1^{v}	2.7888 (8)	Ni1—U1^{ix}	3.4349 (2)
U1—S1	2.7888 (8)	S1—Ni1^{x}	2.4739 (9)
U1—S1^{vi}	3.0088 (8)	S1—U1^{i}	2.7722 (9)
U1—S1^{vii}	3.0088 (8)	S1—U1^{x}	3.0088 (8)
U1—Ni1	3.4349 (2)	S2—Ni1^{x}	2.3386 (4)
U1—Ni1^{viii}	3.4349 (2)	S2—Ni1^{iii}	2.3386 (4)
Ni1—S2^{i}	2.3386 (4)	S2—U1^{iv}	2.6666 (13)
Ni1—S2^{vi}	2.3386 (4)	S2—U1^{xi}	2.7446 (12)
S2^{i}—U1—S2^{ii}	87.32 (2)	S2^{i}—Ni1—S2^{vi}	180.0
S2^{i}—U1—S1^{iii}	141.532 (18)	S2^{i}—Ni1—S1^{ix}	86.82 (3)
S2^{ii}—U1—S1^{iii}	87.85 (3)	S2^{vi}—Ni1—S1^{ix}	93.18 (3)

$S2^{i}$—U1—$S1^{iv}$	141.532 (18)	$S2^{i}$—Ni1—S1	93.18 (3)
$S2^{ii}$—U1—$S1^{iv}$	87.85 (3)	$S2^{vi}$—Ni1—S1	86.82 (3)
$S1^{iii}$—U1—$S1^{iv}$	76.29 (3)	$S1^{ix}$—Ni1—S1	180.00 (4)
$S2^{i}$—U1—$S1^{v}$	78.58 (3)	$S2^{i}$—Ni1—$S1^{i}$	92.11 (4)
$S2^{ii}$—U1—$S1^{v}$	138.939 (19)	$S2^{vi}$—Ni1—$S1^{i}$	87.89 (4)
$S1^{iii}$—U1—$S1^{v}$	80.362 (19)	$S1^{ix}$—Ni1—$S1^{i}$	85.654 (14)
$S1^{iv}$—U1—$S1^{v}$	126.225 (15)	S1—Ni1—$S1^{i}$	94.346 (14)
$S2^{i}$—U1—S1	78.58 (3)	$S2^{i}$—Ni1—$S1^{vi}$	87.89 (4)
$S2^{ii}$—U1—S1	138.939 (19)	$S2^{vi}$—Ni1—$S1^{vi}$	92.11 (4)
$S1^{iii}$—U1—S1	126.225 (15)	$S1^{ix}$—Ni1—$S1^{vi}$	94.346 (14)
$S1^{iv}$—U1—S1	80.362 (19)	S1—Ni1—$S1^{vi}$	85.654 (14)
$S1^{v}$—U1—S1	75.75 (3)	$S1^{i}$—Ni1—$S1^{vi}$	180.0
$S2^{i}$—U1—$S1^{vi}$	71.84 (2)	$S2^{i}$—Ni1—$U1^{ix}$	129.21 (3)
$S2^{ii}$—U1—$S1^{vi}$	69.082 (18)	$S2^{vi}$—Ni1—$U1^{ix}$	50.79 (3)
$S1^{iii}$—U1—$S1^{vi}$	139.987 (15)	$S1^{ix}$—Ni1—$U1^{ix}$	53.55 (2)
$S1^{iv}$—U1—$S1^{vi}$	70.81 (3)	S1—Ni1—$U1^{ix}$	126.45 (2)
$S1^{v}$—U1—$S1^{vi}$	138.102 (15)	$S1^{i}$—Ni1—$U1^{ix}$	58.556 (19)
S1—U1—$S1^{vi}$	69.890 (12)	$S1^{vi}$—Ni1—$U1^{ix}$	121.444 (19)
$S2^{i}$—U1—$S1^{vii}$	71.84 (2)	$S2^{i}$—Ni1—U1	50.79 (3)
$S2^{ii}$—U1—$S1^{vii}$	69.082 (18)	$S2^{vi}$—Ni1—U1	129.21 (3)
$S1^{iii}$—U1—$S1^{vii}$	70.81 (3)	$S1^{ix}$—Ni1—U1	126.45 (2)
$S1^{iv}$—U1—$S1^{vii}$	139.987 (15)	S1—Ni1—U1	53.55 (2)
$S1^{v}$—U1—$S1^{vii}$	69.890 (12)	$S1^{i}$—Ni1—U1	121.444 (19)
S1—U1—$S1^{vii}$	138.102 (15)	$S1^{vi}$—Ni1—U1	58.556 (19)
$S1^{vi}$—U1—$S1^{vii}$	124.80 (3)	$U1^{ix}$—Ni1—U1	180.0
$S2^{i}$—U1—Ni1	42.805 (10)	Ni1—S1—$Ni1^{x}$	139.81 (4)
$S2^{ii}$—U1—Ni1	101.60 (2)	Ni1—S1—$U1^{i}$	87.36 (3)
$S1^{iii}$—U1—Ni1	170.255 (18)	$Ni1^{x}$—S1—$U1^{i}$	132.47 (3)
$S1^{iv}$—U1—Ni1	101.436 (18)	Ni1—S1—U1	82.22 (2)
$S1^{v}$—U1—Ni1	93.784 (19)	$Ni1^{x}$—S1—U1	85.92 (3)
S1—U1—Ni1	44.224 (18)	$U1^{i}$—S1—U1	98.49 (2)
$S1^{vi}$—U1—Ni1	44.546 (18)	Ni1—S1—$U1^{x}$	96.93 (3)
$S1^{vii}$—U1—Ni1	114.642 (18)	$Ni1^{x}$—S1—$U1^{x}$	76.90 (2)
$S2^{i}$—U1—$Ni1^{viii}$	42.805 (10)	$U1^{i}$—S1—$U1^{x}$	109.19 (3)
$S2^{ii}$—U1—$Ni1^{viii}$	101.60 (2)	U1—S1—$U1^{x}$	152.25 (3)
$S1^{iii}$—U1—$Ni1^{viii}$	101.436 (18)	$Ni1^{x}$—S2—$Ni1^{iii}$	138.82 (6)
$S1^{iv}$—U1—$Ni1^{viii}$	170.255 (18)	$Ni1^{x}$—S2—$U1^{iv}$	86.41 (3)
$S1^{v}$—U1—$Ni1^{viii}$	44.224 (18)	$Ni1^{iii}$—S2—$U1^{iv}$	86.41 (3)
S1—U1—$Ni1^{viii}$	93.784 (19)	$Ni1^{x}$—S2—$U1^{xi}$	106.53 (3)
$S1^{vi}$—U1—$Ni1^{viii}$	114.642 (18)	$Ni1^{iii}$—S2—$U1^{xi}$	106.53 (3)
$S1^{vii}$—U1—$Ni1^{viii}$	44.546 (18)	$U1^{iv}$—S2—$U1^{xi}$	136.28 (5)
Ni1—U1—$Ni1^{viii}$	79.190 (5)		

Symmetry codes: (i) $x-1/2, y, -z+1/2$; (ii) $x, y, z-1$; (iii) $x+1/2, -y+1/2, -z+1/2$; (iv) $x+1/2, y, -z+1/2$; (v) $x, -y+1/2, z$; (vi) $-x+1/2, -y, z-1/2$; (vii) $-x+1/2, y+1/2, z-1/2$; (viii) $-x, y+1/2, -z$; (ix) $-x, -y, -z$; (x) $-x+1/2, -y, z+1/2$; (xi) $x, y, z+1$.