Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tris(ethyl carbazate-κ^2N,O)nickel(II) dinitrate

Krishnan Srinivasan,[a] Subbaiah Govindarajan[a] and William T. A. Harrison[b]*

[a]Department of Chemistry, Bharathiar University, Coimbatore 641 046, India, and [b]Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

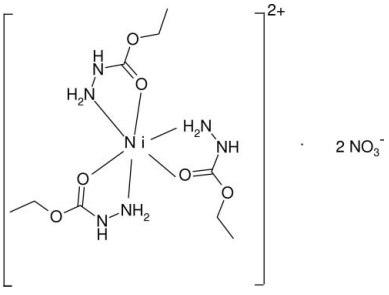
Received 13 November 2007; accepted 14 November 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.051; wR factor = 0.125; data-to-parameter ratio = 21.7.

The asymmetric unit of the title compound, $[Ni(C_3H_8N_2O_2)_3](NO_3)_2$, contains two independent cations, each built up around a *fac*-NiN_3O_3 octahedron, and four nitrate anions. Numerous cation-to-anion N—H···O hydrogen bonds, some of which are bifurcated, help to establish the packing.

Related literature

For related structures, see: Lanfredi *et al.* (1976); Zhang *et al.* (2005); Srinivasan *et al.* (2007).



Experimental

Crystal data

$[Ni(C_3H_8N_2O_2)_3](NO_3)_2$
M_r = 495.07
Monoclinic, $P2_1/n$
a = 14.0580 (8) Å
b = 8.6571 (3) Å
c = 33.6639 (18) Å
β = 92.652 (1)°
V = 4092.6 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.02 mm^{-1}
T = 293 (2) K
0.36 × 0.29 × 0.17 mm

Data collection

Bruker SMART1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.710, T_{max} = 0.845
26981 measured reflections
11856 independent reflections
6057 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.125
S = 0.94
11856 reflections
547 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O1	2.062 (2)	Ni2—O13	2.056 (2)
Ni1—O5	2.065 (2)	Ni2—O15	2.069 (2)
Ni1—N3	2.074 (2)	Ni2—O11	2.071 (2)
Ni1—N5	2.082 (2)	Ni2—N15	2.075 (2)
Ni1—O3	2.0843 (19)	Ni2—N11	2.086 (2)
Ni1—N1	2.103 (2)	Ni2—N13	2.097 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O21^{i}	0.90	2.41	3.158 (3)	140
N1—H1A···O22^{i}	0.90	2.58	3.419 (4)	156
N1—H1B···O21^{ii}	0.90	2.32	3.073 (3)	142
N1—H1B···O23^{ii}	0.90	2.40	3.280 (4)	165
N2—H2···O52^{ii}	0.86	2.14	2.872 (3)	143
N3—H3D···O51	0.90	2.16	3.019 (4)	159
N3—H3E···O41^{i}	0.90	2.32	3.047 (3)	138
N3—H3E···O43^{i}	0.90	2.55	3.435 (4)	170
N4—H4···O31	0.86	2.12	2.951 (3)	162
N5—H5C···O52	0.90	2.01	2.908 (3)	172
N5—H5D···O42	0.90	2.17	3.064 (4)	177
N6—H6···O21	0.86	2.30	3.096 (4)	154
N11—H11A···O31^{iii}	0.90	2.17	3.071 (3)	177
N11—H11B···O22	0.90	2.17	2.989 (3)	151
N12—H12···O51^{iii}	0.86	2.19	2.960 (3)	150
N13—H13D···O23	0.90	2.26	3.046 (4)	146
N13—H13E···O42	0.90	2.30	3.091 (4)	146
N14—H14···O53	0.86	2.25	2.984 (4)	143
N15—H15C···O32	0.90	2.20	3.077 (4)	165
N15—H15D···O41	0.90	2.10	2.951 (4)	157
N16—H16···O31^{iv}	0.86	2.13	2.962 (3)	163
N16—H16···O32^{iv}	0.86	2.40	3.113 (4)	141

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor 1997), *HKL SCALEPACK* and *SORTAV* (Blessing 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SG2208).

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Lanfredi, A. M. M., Tiripicchio, A. & Tiripicchio Camellini, M. (1976). *Cryst. Struct. Commun.* **5**, 827–831.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

  doi:10.1107/S1600536807059053

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Srinivasan, K., Govindarajan, S. & Harrison, W. T. A. (2007). *Acta Cryst.* E**63**, m3028–3029.
Zhang, T.-L., Song, J.-C., Zhang, J.-G., Ma, G.-X. & Yu, K.-B. (2005). *Z. Naturforsch. Teil B*, **60**, 505–510.

supplementary materials

Acta Cryst. (2008). E**64**, m222-m223 [**doi:10.1107/S1600536807059053**]

Tris(ethyl carbazate-$\kappa^2 N,O$)nickel(II) dinitrate

K. Srinivasan, S. Govindarajan and W. T. A. Harrison

Comment

The title compound, (I), is isostructural with its zinc congener (Zhang *et al.*, 2005). The cobalt-containing compound was also reported to have the same structure by Zhang and co-workers. We have recently observed a supercell for the latter phase (Srinivasan *et al.*, 2007).

The two $[Ni(C_3H_8N_2O_2)_3]^{2+}$ complex cations in (I) are similar (Fig. 1) and are each built up around a slightly distorted *fac*-NiN_3O_3 octahedral core (Table 1). A five-membered –Ni—N—N—C—O– chelate ring arises for each of the six distinct N,*O*-bidentate ligands.

The crystal packing for (I) is consolidated by a large number of cation-to-anion N—H···O hydrogen bonds (Table 2), a number of which are bifurcated.

The crysatl structure of the $[Ni(C_3H_8N_2O_2)_3]^{2+}$ complex cation accompanied by chloride ions was described some time ago (Lanfredi *et al.*, 1976).

Experimental

Ethyl carbazate (0.208 g, 0.002 mol) was added to an aqueous solution (25 ml) containing formic acid (85%, 0.08 ml). To this solution was added nickel nitrate hexahydrate (0.291 g, 0.001 mol) dissolved in 50 ml of double distilled water. The resulting green solution was concentrated over a water bath to about 15 ml and kept for crystallization at room temperature. Blue blocks of (I) obtained after a week were separated and washed with ethanol and air dried.

Refinement

The diffraction data were carefully examined, but no trace of a supercell was discernable. The hydrogen atoms were geometrically placed (N—H = 0.86–0.90 Å, C—H = 0.96–0.97 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(N,*C*) or 1.5U_{eq}(methyl C).

Figures

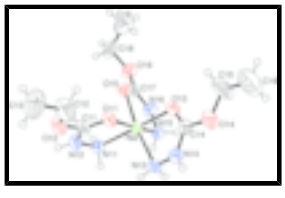


Fig. 1. View of the Ni2-containing complex cation in (I) shoiwng 50% displacement ellipsoids (arbitrary spheres for the H atoms). The C-bound H atoms are omitted for clarity.

Tris(ethyl carbazate-κ^2*N*,*O*)nickel(II) dinitrate

Crystal data

$[Ni(C_3H_8N_2O_2)_3](NO_3)_2$	F_{000} = 2064
M_r = 495.07	D_x = 1.607 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 6204 reflections
a = 14.0580 (8) Å	θ = 4.3–28.0º
b = 8.6571 (3) Å	μ = 1.02 mm^{-1}
c = 33.6639 (18) Å	T = 293 (2) K
β = 92.652 (1)º	Block, blue
V = 4092.6 (3) Å^3	0.36 × 0.29 × 0.17 mm
Z = 8	

Data collection

Bruker SMART1000 CCD diffractometer	11856 independent reflections
Radiation source: fine-focus sealed tube	6057 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.042
T = 293(2) K	θ_{max} = 30.2º
ω scans	θ_{min} = 4.3º
Absorption correction: multi-scan (SADABS; Bruker, 2003)	h = −19→18
T_{min} = 0.710, T_{max} = 0.845	k = −6→12
26981 measured reflections	l = −47→47

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.051	H-atom parameters constrained
$wR(F^2)$ = 0.125	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.94	$(\Delta/\sigma)_{max}$ = 0.001
11856 reflections	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
547 parameters	$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. ? ?

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}
Ni1	0.81839 (3)	0.75534 (4)	0.154396 (10)	0.04181 (10)
C1	0.9239 (2)	1.0247 (4)	0.15603 (9)	0.0508 (7)
C2	1.0145 (4)	1.1639 (6)	0.10942 (15)	0.1108 (17)
H2A	1.0830	1.1774	0.1105	0.133*
H2B	0.9993	1.0733	0.0934	0.133*
C3	0.9722 (6)	1.2897 (8)	0.09249 (18)	0.159 (3)
H3A	0.9989	1.3094	0.0673	0.239*
H3B	0.9826	1.3775	0.1095	0.239*
H3C	0.9050	1.2713	0.0886	0.239*
N1	0.82926 (19)	0.9099 (3)	0.20261 (7)	0.0487 (6)
H1A	0.7723	0.9529	0.2067	0.058*
H1B	0.8492	0.8599	0.2249	0.058*
N2	0.8955 (2)	1.0241 (3)	0.19293 (7)	0.0552 (7)
H2	0.9165	1.0904	0.2102	0.066*
O1	0.90039 (15)	0.9274 (2)	0.13099 (6)	0.0508 (5)
O2	0.9818 (2)	1.1409 (3)	0.14981 (8)	0.0813 (8)
C4	0.7404 (2)	0.6828 (3)	0.07980 (9)	0.0511 (7)
C5	0.7692 (3)	0.5000 (5)	0.02964 (12)	0.0849 (13)
H5A	0.7287	0.4380	0.0118	0.102*
H5B	0.7908	0.4353	0.0518	0.102*
C6	0.8520 (5)	0.5551 (7)	0.00840 (16)	0.135 (2)
H6A	0.8891	0.4683	0.0004	0.202*
H6B	0.8905	0.6206	0.0256	0.202*
H6C	0.8304	0.6124	−0.0147	0.202*
N3	0.69577 (18)	0.8548 (3)	0.12911 (7)	0.0484 (6)
H3D	0.6459	0.8359	0.1443	0.058*
H3E	0.7031	0.9577	0.1271	0.058*
N4	0.6800 (2)	0.7887 (3)	0.09118 (7)	0.0574 (7)
H4	0.6324	0.8167	0.0759	0.069*
O3	0.81106 (15)	0.6415 (2)	0.09979 (6)	0.0500 (5)
O4	0.7153 (2)	0.6283 (3)	0.04421 (6)	0.0738 (7)
C7	0.9102 (3)	0.5165 (4)	0.19524 (10)	0.0562 (8)
C8	1.0668 (4)	0.4764 (7)	0.2236 (2)	0.129 (2)
H8A	1.0672	0.5882	0.2254	0.155*
H8B	1.0901	0.4341	0.2489	0.155*

C9	1.1191 (6)	0.4303 (10)	0.1952 (3)	0.188 (4)
H9A	1.1842	0.4580	0.2014	0.282*
H9B	1.0977	0.4787	0.1707	0.282*
H9C	1.1140	0.3202	0.1925	0.282*
N5	0.75100 (18)	0.5674 (3)	0.17952 (7)	0.0500 (6)
H5C	0.7105	0.6003	0.1976	0.060*
H5D	0.7176	0.5144	0.1606	0.060*
N6	0.8211 (2)	0.4720 (3)	0.19776 (8)	0.0572 (7)
H6	0.8065	0.3887	0.2100	0.069*
O5	0.93445 (15)	0.6349 (2)	0.17806 (6)	0.0535 (5)
O6	0.9692 (2)	0.4191 (3)	0.21322 (10)	0.0970 (10)
Ni2	0.36902 (3)	0.22636 (4)	0.106643 (10)	0.04364 (11)
C11	0.3169 (2)	0.0113 (4)	0.16235 (9)	0.0523 (8)
C12	0.1854 (3)	−0.0161 (6)	0.20373 (15)	0.1049 (17)
H12A	0.1970	0.0778	0.2189	0.126*
H12B	0.1419	0.0081	0.1814	0.126*
C13	0.1443 (4)	−0.1278 (6)	0.22789 (18)	0.130 (2)
H13A	0.0887	−0.0854	0.2393	0.196*
H13B	0.1894	−0.1578	0.2487	0.196*
H13C	0.1266	−0.2165	0.2121	0.196*
N11	0.45074 (17)	0.0358 (3)	0.12481 (7)	0.0460 (6)
H11A	0.4627	−0.0241	0.1038	0.055*
H11B	0.5066	0.0670	0.1362	0.055*
N12	0.39883 (19)	−0.0466 (3)	0.15207 (8)	0.0565 (7)
H12	0.4197	−0.1326	0.1619	0.068*
O11	0.28303 (15)	0.1324 (2)	0.14873 (6)	0.0532 (5)
O12	0.27538 (17)	−0.0737 (3)	0.18905 (8)	0.0753 (7)
C14	0.2889 (2)	0.5054 (4)	0.12510 (10)	0.0546 (8)
C15	0.1668 (5)	0.6550 (7)	0.09490 (19)	0.150 (3)
H15A	0.2000	0.6535	0.0703	0.180*
H15B	0.1214	0.5705	0.0940	0.180*
C16	0.1206 (6)	0.7853 (9)	0.0973 (2)	0.181 (3)
H16A	0.0767	0.7955	0.0747	0.272*
H16B	0.1649	0.8697	0.0977	0.272*
H16C	0.0861	0.7865	0.1213	0.272*
N13	0.42753 (18)	0.3833 (3)	0.14845 (7)	0.0486 (6)
H13D	0.4434	0.3348	0.1715	0.058*
H13E	0.4800	0.4278	0.1393	0.058*
N14	0.35665 (19)	0.4951 (3)	0.15428 (8)	0.0544 (6)
H14	0.3569	0.5527	0.1751	0.065*
O13	0.27628 (15)	0.4088 (2)	0.09905 (6)	0.0567 (5)
O14	0.2364 (2)	0.6297 (3)	0.12846 (8)	0.0846 (8)
C17	0.3493 (3)	0.1147 (3)	0.03006 (9)	0.0521 (8)
C18	0.2543 (4)	−0.0744 (5)	−0.00350 (12)	0.0909 (14)
H18A	0.2562	−0.1251	0.0222	0.109*
H18B	0.2662	−0.1519	−0.0235	0.109*
C19	0.1596 (4)	−0.0083 (7)	−0.01148 (19)	0.143 (2)
H19A	0.1121	−0.0859	−0.0077	0.215*
H19B	0.1543	0.0283	−0.0384	0.215*

H19C	0.1502	0.0762	0.0064	0.215*
N15	0.45223 (19)	0.2944 (3)	0.06042 (7)	0.0507 (6)
H15C	0.4441	0.3958	0.0554	0.061*
H15D	0.5142	0.2774	0.0668	0.061*
N16	0.4231 (2)	0.2065 (3)	0.02672 (7)	0.0591 (7)
H16	0.4524	0.2126	0.0049	0.071*
O15	0.30548 (16)	0.0995 (2)	0.06056 (6)	0.0540 (5)
O16	0.32763 (19)	0.0407 (3)	−0.00376 (6)	0.0726 (7)
N21	0.6243 (2)	0.1811 (3)	0.20952 (7)	0.0493 (6)
O21	0.70396 (17)	0.1946 (3)	0.22680 (7)	0.0665 (6)
O22	0.60891 (19)	0.0714 (3)	0.18656 (7)	0.0773 (7)
O23	0.5623 (2)	0.2750 (4)	0.21627 (8)	0.0940 (9)
N31	0.4518 (2)	0.7144 (3)	0.05618 (8)	0.0550 (6)
O31	0.49163 (16)	0.8417 (2)	0.05117 (6)	0.0578 (5)
O32	0.4373 (2)	0.6266 (3)	0.02821 (8)	0.0954 (9)
O33	0.4328 (3)	0.6772 (4)	0.08930 (9)	0.1372 (15)
N41	0.6723 (2)	0.2646 (3)	0.11276 (8)	0.0543 (6)
O41	0.63393 (18)	0.1611 (3)	0.09159 (7)	0.0688 (6)
O42	0.63042 (17)	0.3890 (3)	0.11677 (8)	0.0743 (7)
O43	0.7498 (2)	0.2417 (3)	0.12965 (9)	0.0895 (8)
N51	0.5319 (2)	0.6816 (3)	0.20948 (8)	0.0537 (6)
O51	0.53746 (17)	0.7060 (3)	0.17313 (7)	0.0660 (6)
O52	0.60552 (17)	0.6768 (3)	0.23136 (6)	0.0670 (6)
O53	0.45284 (19)	0.6607 (4)	0.22271 (9)	0.0893 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0468 (2)	0.0397 (2)	0.03881 (18)	0.00573 (16)	0.00038 (14)	0.00073 (15)
C1	0.056 (2)	0.0479 (18)	0.0477 (17)	0.0015 (14)	−0.0029 (14)	0.0069 (14)
C2	0.157 (5)	0.078 (3)	0.100 (3)	−0.026 (3)	0.036 (3)	0.015 (3)
C3	0.215 (8)	0.155 (6)	0.108 (4)	0.041 (5)	0.005 (5)	0.041 (4)
N1	0.0639 (17)	0.0460 (14)	0.0365 (12)	0.0081 (12)	0.0040 (11)	0.0040 (10)
N2	0.0730 (19)	0.0509 (16)	0.0413 (14)	−0.0059 (13)	−0.0011 (13)	−0.0037 (11)
O1	0.0630 (14)	0.0492 (12)	0.0404 (11)	−0.0011 (10)	0.0058 (10)	0.0006 (9)
O2	0.104 (2)	0.0658 (17)	0.0755 (17)	−0.0298 (15)	0.0178 (15)	−0.0017 (13)
C4	0.068 (2)	0.0428 (17)	0.0418 (16)	0.0023 (15)	−0.0059 (15)	0.0009 (13)
C5	0.121 (4)	0.062 (3)	0.070 (2)	0.016 (2)	−0.014 (2)	−0.0215 (19)
C6	0.164 (6)	0.136 (5)	0.108 (4)	0.035 (4)	0.046 (4)	−0.005 (4)
N3	0.0560 (16)	0.0452 (14)	0.0440 (13)	0.0098 (11)	0.0010 (11)	0.0010 (11)
N4	0.0665 (18)	0.0561 (17)	0.0478 (14)	0.0159 (13)	−0.0152 (12)	−0.0044 (12)
O3	0.0578 (13)	0.0470 (12)	0.0448 (11)	0.0087 (10)	−0.0013 (10)	−0.0052 (9)
O4	0.103 (2)	0.0658 (16)	0.0503 (13)	0.0144 (14)	−0.0208 (13)	−0.0160 (11)
C7	0.063 (2)	0.0385 (17)	0.066 (2)	0.0086 (15)	−0.0067 (17)	0.0040 (15)
C8	0.088 (4)	0.116 (4)	0.184 (6)	0.015 (3)	−0.006 (4)	0.074 (4)
C9	0.149 (7)	0.209 (8)	0.211 (8)	−0.043 (6)	0.074 (6)	−0.073 (7)
N5	0.0499 (15)	0.0462 (14)	0.0543 (14)	0.0042 (11)	0.0049 (12)	0.0054 (11)
N6	0.0617 (18)	0.0450 (15)	0.0650 (17)	0.0019 (13)	0.0032 (14)	0.0135 (12)

O5	0.0494 (13)	0.0451 (12)	0.0654 (13)	0.0044 (9)	−0.0045 (10)	0.0090 (10)
O6	0.0696 (18)	0.0669 (17)	0.152 (3)	0.0096 (14)	−0.0220 (18)	0.0428 (17)
Ni2	0.0471 (2)	0.0433 (2)	0.04003 (19)	0.00219 (16)	−0.00265 (15)	0.00044 (15)
C11	0.052 (2)	0.056 (2)	0.0480 (17)	−0.0015 (15)	−0.0010 (15)	0.0084 (14)
C12	0.065 (3)	0.130 (4)	0.122 (4)	0.016 (3)	0.035 (3)	0.055 (3)
C13	0.122 (4)	0.106 (4)	0.170 (5)	−0.002 (3)	0.074 (4)	0.029 (4)
N11	0.0466 (14)	0.0475 (14)	0.0440 (13)	0.0017 (11)	0.0023 (11)	−0.0042 (11)
N12	0.0534 (17)	0.0475 (15)	0.0687 (17)	0.0072 (12)	0.0046 (13)	0.0159 (13)
O11	0.0489 (12)	0.0590 (14)	0.0520 (12)	0.0097 (10)	0.0053 (10)	0.0113 (10)
O12	0.0631 (16)	0.0813 (17)	0.0829 (17)	0.0032 (13)	0.0171 (13)	0.0314 (14)
C14	0.058 (2)	0.0467 (19)	0.0591 (19)	0.0036 (15)	−0.0003 (16)	−0.0006 (15)
C15	0.152 (5)	0.112 (4)	0.176 (6)	0.082 (4)	−0.080 (5)	−0.036 (4)
C16	0.210 (8)	0.164 (7)	0.164 (7)	0.070 (6)	−0.052 (6)	0.009 (5)
N13	0.0511 (15)	0.0504 (15)	0.0438 (13)	0.0014 (11)	−0.0036 (11)	−0.0037 (11)
N14	0.0571 (17)	0.0492 (16)	0.0566 (15)	0.0047 (12)	0.0006 (13)	−0.0095 (12)
O13	0.0570 (14)	0.0523 (13)	0.0592 (13)	0.0072 (10)	−0.0150 (11)	0.0006 (10)
O14	0.0826 (19)	0.0653 (17)	0.104 (2)	0.0302 (14)	−0.0172 (16)	−0.0148 (14)
C17	0.071 (2)	0.0429 (17)	0.0410 (16)	0.0004 (15)	−0.0097 (15)	0.0034 (13)
C18	0.137 (4)	0.063 (3)	0.070 (3)	−0.035 (3)	−0.013 (3)	−0.010 (2)
C19	0.124 (5)	0.134 (5)	0.167 (6)	−0.056 (4)	−0.046 (4)	0.026 (4)
N15	0.0592 (16)	0.0478 (15)	0.0447 (13)	−0.0055 (12)	−0.0034 (11)	0.0015 (11)
N16	0.081 (2)	0.0618 (18)	0.0346 (12)	−0.0138 (15)	0.0013 (12)	−0.0011 (11)
O15	0.0633 (14)	0.0526 (13)	0.0456 (12)	−0.0088 (10)	−0.0029 (10)	−0.0015 (9)
O16	0.107 (2)	0.0668 (16)	0.0431 (12)	−0.0217 (14)	−0.0077 (12)	−0.0066 (11)
N21	0.0588 (17)	0.0517 (16)	0.0372 (13)	0.0036 (13)	0.0005 (12)	−0.0029 (11)
O21	0.0641 (15)	0.0782 (17)	0.0555 (13)	−0.0017 (12)	−0.0166 (11)	−0.0032 (11)
O22	0.0901 (19)	0.0786 (18)	0.0626 (15)	−0.0167 (14)	−0.0026 (13)	−0.0278 (13)
O23	0.091 (2)	0.104 (2)	0.0855 (19)	0.0506 (18)	−0.0087 (15)	−0.0140 (16)
N31	0.0649 (18)	0.0522 (17)	0.0476 (15)	−0.0040 (13)	0.0011 (13)	−0.0021 (13)
O31	0.0696 (15)	0.0432 (12)	0.0606 (13)	−0.0031 (11)	0.0027 (11)	0.0028 (10)
O32	0.160 (3)	0.0598 (17)	0.0659 (16)	−0.0157 (17)	−0.0025 (17)	−0.0126 (13)
O33	0.228 (4)	0.115 (3)	0.072 (2)	−0.074 (3)	0.053 (2)	−0.0056 (18)
N41	0.0540 (17)	0.0521 (17)	0.0572 (15)	−0.0012 (14)	0.0091 (13)	0.0035 (13)
O41	0.0794 (17)	0.0554 (15)	0.0709 (15)	0.0011 (12)	−0.0043 (13)	−0.0107 (12)
O42	0.0631 (16)	0.0480 (14)	0.111 (2)	0.0075 (12)	−0.0006 (14)	−0.0144 (13)
O43	0.0623 (17)	0.091 (2)	0.113 (2)	0.0121 (14)	−0.0181 (16)	−0.0019 (16)
N51	0.0582 (18)	0.0486 (16)	0.0544 (16)	0.0097 (12)	0.0037 (14)	−0.0034 (12)
O51	0.0750 (16)	0.0711 (16)	0.0505 (13)	−0.0006 (12)	−0.0125 (11)	0.0134 (11)
O52	0.0616 (15)	0.0911 (18)	0.0472 (12)	0.0203 (13)	−0.0099 (11)	0.0027 (11)
O53	0.0603 (17)	0.112 (2)	0.098 (2)	−0.0084 (15)	0.0240 (15)	−0.0276 (17)

Geometric parameters (Å, °)

Ni1—O1	2.062 (2)	C11—O11	1.231 (4)
Ni1—O5	2.065 (2)	C11—N12	1.317 (4)
Ni1—N3	2.074 (2)	C11—O12	1.319 (4)
Ni1—N5	2.082 (2)	C12—C13	1.405 (6)
Ni1—O3	2.0843 (19)	C12—O12	1.466 (5)
Ni1—N1	2.103 (2)	C12—H12A	0.9700

C1—O1	1.226 (4)	C12—H12B	0.9700
C1—O2	1.317 (4)	C13—H13A	0.9600
C1—N2	1.322 (4)	C13—H13B	0.9600
C2—C3	1.354 (7)	C13—H13C	0.9600
C2—O2	1.469 (5)	N11—N12	1.395 (3)
C2—H2A	0.9700	N11—H11A	0.9000
C2—H2B	0.9700	N11—H11B	0.9000
C3—H3A	0.9600	N12—H12	0.8600
C3—H3B	0.9600	C14—O13	1.218 (4)
C3—H3C	0.9600	C14—O14	1.313 (4)
N1—N2	1.406 (3)	C14—N14	1.339 (4)
N1—H1A	0.9000	C15—C16	1.307 (7)
N1—H1B	0.9000	C15—O14	1.476 (5)
N2—H2	0.8600	C15—H15A	0.9700
C4—O3	1.227 (3)	C15—H15B	0.9700
C4—N4	1.318 (4)	C16—H16A	0.9600
C4—O4	1.321 (3)	C16—H16B	0.9600
C5—O4	1.443 (4)	C16—H16C	0.9600
C5—C6	1.474 (7)	N13—N14	1.409 (3)
C5—H5A	0.9700	N13—H13D	0.9000
C5—H5B	0.9700	N13—H13E	0.9000
C6—H6A	0.9600	N14—H14	0.8600
C6—H6B	0.9600	C17—O15	1.228 (4)
C6—H6C	0.9600	C17—N16	1.316 (4)
N3—N4	1.407 (3)	C17—O16	1.329 (4)
N3—H3D	0.9000	C18—O16	1.434 (5)
N3—H3E	0.9000	C18—C19	1.463 (7)
N4—H4	0.8600	C18—H18A	0.9700
C7—O5	1.233 (4)	C18—H18B	0.9700
C7—O6	1.311 (4)	C19—H19A	0.9600
C7—N6	1.316 (4)	C19—H19B	0.9600
C8—C9	1.294 (8)	C19—H19C	0.9600
C8—O6	1.485 (6)	N15—N16	1.411 (3)
C8—H8A	0.9700	N15—H15C	0.9000
C8—H8B	0.9700	N15—H15D	0.9000
C9—H9A	0.9600	N16—H16	0.8600
C9—H9B	0.9600	N21—O23	1.222 (3)
C9—H9C	0.9600	N21—O22	1.237 (3)
N5—N6	1.405 (3)	N21—O21	1.243 (3)
N5—H5C	0.9000	N31—O33	1.202 (3)
N5—H5D	0.9000	N31—O32	1.220 (3)
N6—H6	0.8600	N31—O31	1.251 (3)
Ni2—O13	2.056 (2)	N41—O43	1.222 (3)
Ni2—O15	2.069 (2)	N41—O42	1.237 (3)
Ni2—O11	2.071 (2)	N41—O41	1.251 (3)
Ni2—N15	2.075 (2)	N51—O53	1.230 (3)
Ni2—N11	2.086 (2)	N51—O52	1.243 (3)
Ni2—N13	2.097 (2)	N51—O51	1.248 (3)
O1—Ni1—O5	93.81 (8)	O13—Ni2—N11	168.92 (9)

O1—Ni1—N3	90.69 (9)	O15—Ni2—N11	90.74 (9)
O5—Ni1—N3	174.19 (9)	O11—Ni2—N11	79.61 (9)
O1—Ni1—N5	173.06 (9)	N15—Ni2—N11	97.04 (10)
O5—Ni1—N5	79.34 (9)	O13—Ni2—N13	79.20 (9)
N3—Ni1—N5	96.08 (10)	O15—Ni2—N13	171.66 (9)
O1—Ni1—O3	90.59 (8)	O11—Ni2—N13	91.06 (9)
O5—Ni1—O3	96.16 (8)	N15—Ni2—N13	95.86 (10)
N3—Ni1—O3	80.10 (9)	N11—Ni2—N13	97.00 (9)
N5—Ni1—O3	89.08 (9)	O11—C11—N12	123.6 (3)
O1—Ni1—N1	79.25 (9)	O11—C11—O12	123.6 (3)
O5—Ni1—N1	89.74 (9)	N12—C11—O12	112.8 (3)
N3—Ni1—N1	94.71 (10)	C13—C12—O12	110.2 (4)
N5—Ni1—N1	101.64 (10)	C13—C12—H12A	109.6
O3—Ni1—N1	168.59 (8)	O12—C12—H12A	109.6
O1—C1—O2	124.3 (3)	C13—C12—H12B	109.6
O1—C1—N2	124.0 (3)	O12—C12—H12B	109.6
O2—C1—N2	111.6 (3)	H12A—C12—H12B	108.1
C3—C2—O2	110.4 (5)	C12—C13—H13A	109.5
C3—C2—H2A	109.6	C12—C13—H13B	109.5
O2—C2—H2A	109.6	H13A—C13—H13B	109.5
C3—C2—H2B	109.6	C12—C13—H13C	109.5
O2—C2—H2B	109.6	H13A—C13—H13C	109.5
H2A—C2—H2B	108.1	H13B—C13—H13C	109.5
C2—C3—H3A	109.5	N12—N11—Ni2	107.44 (17)
C2—C3—H3B	109.5	N12—N11—H11A	110.2
H3A—C3—H3B	109.5	Ni2—N11—H11A	110.2
C2—C3—H3C	109.5	N12—N11—H11B	110.2
H3A—C3—H3C	109.5	Ni2—N11—H11B	110.2
H3B—C3—H3C	109.5	H11A—N11—H11B	108.5
N2—N1—Ni1	107.07 (16)	C11—N12—N11	118.0 (2)
N2—N1—H1A	110.3	C11—N12—H12	121.0
Ni1—N1—H1A	110.3	N11—N12—H12	121.0
N2—N1—H1B	110.3	C11—O11—Ni2	111.2 (2)
Ni1—N1—H1B	110.3	C11—O12—C12	117.1 (3)
H1A—N1—H1B	108.6	O13—C14—O14	124.1 (3)
C1—N2—N1	116.9 (2)	O13—C14—N14	123.8 (3)
C1—N2—H2	121.5	O14—C14—N14	112.0 (3)
N1—N2—H2	121.5	C16—C15—O14	113.3 (5)
C1—O1—Ni1	111.78 (19)	C16—C15—H15A	108.9
C1—O2—C2	118.2 (3)	O14—C15—H15A	108.9
O3—C4—N4	124.0 (3)	C16—C15—H15B	108.9
O3—C4—O4	124.6 (3)	O14—C15—H15B	108.9
N4—C4—O4	111.4 (3)	H15A—C15—H15B	107.7
O4—C5—C6	110.8 (4)	C15—C16—H16A	109.5
O4—C5—H5A	109.5	C15—C16—H16B	109.5
C6—C5—H5A	109.5	H16A—C16—H16B	109.5
O4—C5—H5B	109.5	C15—C16—H16C	109.5
C6—C5—H5B	109.5	H16A—C16—H16C	109.5
H5A—C5—H5B	108.1	H16B—C16—H16C	109.5

C5—C6—H6A	109.5	N14—N13—Ni2	106.29 (17)
C5—C6—H6B	109.5	N14—N13—H13D	110.5
H6A—C6—H6B	109.5	Ni2—N13—H13D	110.5
C5—C6—H6C	109.5	N14—N13—H13E	110.5
H6A—C6—H6C	109.5	Ni2—N13—H13E	110.5
H6B—C6—H6C	109.5	H13D—N13—H13E	108.7
N4—N3—Ni1	107.26 (17)	C14—N14—N13	115.3 (2)
N4—N3—H3D	110.3	C14—N14—H14	122.4
Ni1—N3—H3D	110.3	N13—N14—H14	122.4
N4—N3—H3E	110.3	C14—O13—Ni2	111.5 (2)
Ni1—N3—H3E	110.3	C14—O14—C15	114.3 (3)
H3D—N3—H3E	108.5	O15—C17—N16	124.3 (3)
C4—N4—N3	118.0 (2)	O15—C17—O16	124.1 (3)
C4—N4—H4	121.0	N16—C17—O16	111.6 (3)
N3—N4—H4	121.0	O16—C18—C19	112.0 (4)
C4—O3—Ni1	110.56 (19)	O16—C18—H18A	109.2
C4—O4—C5	117.5 (3)	C19—C18—H18A	109.2
O5—C7—O6	124.6 (3)	O16—C18—H18B	109.2
O5—C7—N6	123.9 (3)	C19—C18—H18B	109.2
O6—C7—N6	111.5 (3)	H18A—C18—H18B	107.9
C9—C8—O6	105.9 (7)	C18—C19—H19A	109.5
C9—C8—H8A	110.5	C18—C19—H19B	109.5
O6—C8—H8A	110.5	H19A—C19—H19B	109.5
C9—C8—H8B	110.5	C18—C19—H19C	109.5
O6—C8—H8B	110.5	H19A—C19—H19C	109.5
H8A—C8—H8B	108.7	H19B—C19—H19C	109.5
C8—C9—H9A	109.5	N16—N15—Ni2	107.28 (18)
C8—C9—H9B	109.5	N16—N15—H15C	110.3
H9A—C9—H9B	109.5	Ni2—N15—H15C	110.3
C8—C9—H9C	109.5	N16—N15—H15D	110.3
H9A—C9—H9C	109.5	Ni2—N15—H15D	110.3
H9B—C9—H9C	109.5	H15C—N15—H15D	108.5
N6—N5—Ni1	108.28 (18)	C17—N16—N15	117.2 (2)
N6—N5—H5C	110.0	C17—N16—H16	121.4
Ni1—N5—H5C	110.0	N15—N16—H16	121.4
N6—N5—H5D	110.0	C17—O15—Ni2	110.7 (2)
Ni1—N5—H5D	110.0	C17—O16—C18	117.8 (3)
H5C—N5—H5D	108.4	O23—N21—O22	121.4 (3)
C7—N6—N5	116.8 (3)	O23—N21—O21	119.1 (3)
C7—N6—H6	121.6	O22—N21—O21	119.5 (3)
N5—N6—H6	121.6	O33—N31—O32	120.8 (3)
C7—O5—Ni1	111.7 (2)	O33—N31—O31	118.8 (3)
C7—O6—C8	116.9 (3)	O32—N31—O31	120.3 (3)
O13—Ni2—O15	93.74 (9)	O43—N41—O42	120.6 (3)
O13—Ni2—O11	90.00 (9)	O43—N41—O41	120.0 (3)
O15—Ni2—O11	93.39 (9)	O42—N41—O41	119.4 (3)
O13—Ni2—N15	93.71 (10)	O53—N51—O52	121.5 (3)
O15—Ni2—N15	80.05 (9)	O53—N51—O51	118.6 (3)
O11—Ni2—N15	172.65 (9)	O52—N51—O51	119.9 (3)

O1—Ni1—N1—N2	−8.35 (17)	O13—Ni2—N11—N12	24.1 (6)
O5—Ni1—N1—N2	85.58 (18)	O15—Ni2—N11—N12	−89.82 (18)
N3—Ni1—N1—N2	−98.16 (18)	O11—Ni2—N11—N12	3.49 (18)
N5—Ni1—N1—N2	164.63 (17)	N15—Ni2—N11—N12	−169.89 (18)
O3—Ni1—N1—N2	−35.8 (6)	N13—Ni2—N11—N12	93.28 (19)
O1—C1—N2—N1	−4.5 (5)	O11—C11—N12—N11	1.3 (5)
O2—C1—N2—N1	176.8 (3)	O12—C11—N12—N11	−178.2 (3)
Ni1—N1—N2—C1	9.5 (3)	Ni2—N11—N12—C11	−3.7 (3)
O2—C1—O1—Ni1	175.0 (3)	N12—C11—O11—Ni2	2.1 (4)
N2—C1—O1—Ni1	−3.6 (4)	O12—C11—O11—Ni2	−178.6 (3)
O5—Ni1—O1—C1	−82.2 (2)	O13—Ni2—O11—C11	−179.2 (2)
N3—Ni1—O1—C1	101.5 (2)	O15—Ni2—O11—C11	87.0 (2)
O3—Ni1—O1—C1	−178.4 (2)	N11—Ni2—O11—C11	−3.1 (2)
N1—Ni1—O1—C1	6.8 (2)	N13—Ni2—O11—C11	−100.0 (2)
O1—C1—O2—C2	5.4 (5)	O11—C11—O12—C12	−1.8 (5)
N2—C1—O2—C2	−175.9 (4)	N12—C11—O12—C12	177.6 (3)
C3—C2—O2—C1	107.9 (5)	C13—C12—O12—C11	172.5 (4)
O1—Ni1—N3—N4	90.63 (19)	O13—Ni2—N13—N14	16.10 (17)
N5—Ni1—N3—N4	−87.85 (19)	O11—Ni2—N13—N14	−73.70 (18)
O3—Ni1—N3—N4	0.15 (18)	N15—Ni2—N13—N14	108.78 (18)
N1—Ni1—N3—N4	169.90 (19)	N11—Ni2—N13—N14	−153.36 (17)
O3—C4—N4—N3	−2.2 (5)	O13—C14—N14—N13	13.9 (5)
O4—C4—N4—N3	178.2 (3)	O14—C14—N14—N13	−167.6 (3)
Ni1—N3—N4—C4	0.9 (3)	Ni2—N13—N14—C14	−20.5 (3)
N4—C4—O3—Ni1	2.2 (4)	O14—C14—O13—Ni2	−176.5 (3)
O4—C4—O3—Ni1	−178.3 (3)	N14—C14—O13—Ni2	1.8 (4)
O1—Ni1—O3—C4	−91.8 (2)	O15—Ni2—O13—C14	173.9 (2)
O5—Ni1—O3—C4	174.3 (2)	O11—Ni2—O13—C14	80.5 (2)
N3—Ni1—O3—C4	−1.2 (2)	N15—Ni2—O13—C14	−105.8 (2)
N5—Ni1—O3—C4	95.2 (2)	N11—Ni2—O13—C14	60.3 (6)
N1—Ni1—O3—C4	−64.9 (5)	N13—Ni2—O13—C14	−10.5 (2)
O3—C4—O4—C5	6.8 (5)	O13—C14—O14—C15	−7.3 (6)
N4—C4—O4—C5	−173.7 (3)	N14—C14—O14—C15	174.2 (4)
C6—C5—O4—C4	−88.4 (5)	C16—C15—O14—C14	−174.9 (6)
O5—Ni1—N5—N6	0.67 (18)	O13—Ni2—N15—N16	−98.25 (19)
N3—Ni1—N5—N6	177.06 (18)	O15—Ni2—N15—N16	−5.10 (18)
O3—Ni1—N5—N6	97.12 (18)	N11—Ni2—N15—N16	84.42 (19)
N1—Ni1—N5—N6	−86.84 (19)	N13—Ni2—N15—N16	−177.75 (19)
O5—C7—N6—N5	0.0 (5)	O15—C17—N16—N15	−1.0 (5)
O6—C7—N6—N5	−180.0 (3)	O16—C17—N16—N15	178.7 (2)
Ni1—N5—N6—C7	−0.6 (3)	Ni2—N15—N16—C17	5.1 (3)
O6—C7—O5—Ni1	−179.4 (3)	N16—C17—O15—Ni2	−3.8 (4)
N6—C7—O5—Ni1	0.6 (4)	O16—C17—O15—Ni2	176.6 (2)
O1—Ni1—O5—C7	−179.6 (2)	O13—Ni2—O15—C17	98.0 (2)
N5—Ni1—O5—C7	−0.7 (2)	O11—Ni2—O15—C17	−171.7 (2)
O3—Ni1—O5—C7	−88.6 (2)	N15—Ni2—O15—C17	4.9 (2)
N1—Ni1—O5—C7	101.2 (2)	N11—Ni2—O15—C17	−92.1 (2)
O5—C7—O6—C8	18.3 (6)	O15—C17—O16—C18	−6.1 (5)
N6—C7—O6—C8	−161.7 (4)	N16—C17—O16—C18	174.2 (3)

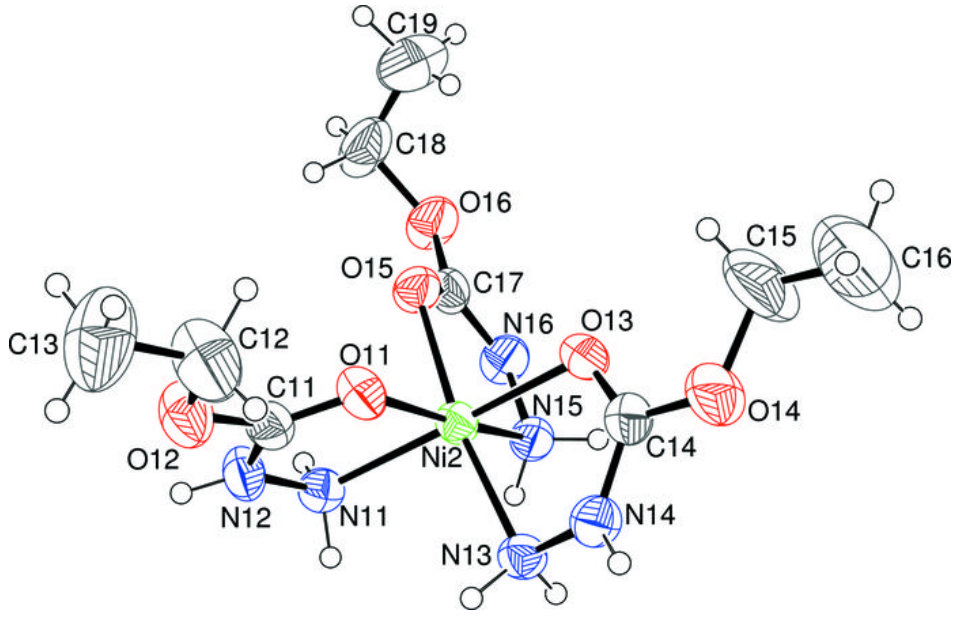
C9—C8—O6—C7	−96.9 (6)	C19—C18—O16—C17	87.5 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O21^{i}	0.90	2.41	3.158 (3)	140
N1—H1A···O22^{i}	0.90	2.58	3.419 (4)	156
N1—H1B···O21^{ii}	0.90	2.32	3.073 (3)	142
N1—H1B···O23^{ii}	0.90	2.40	3.280 (4)	165
N2—H2···O52^{ii}	0.86	2.14	2.872 (3)	143
N3—H3D···O51	0.90	2.16	3.019 (4)	159
N3—H3E···O41^{i}	0.90	2.32	3.047 (3)	138
N3—H3E···O43^{i}	0.90	2.55	3.435 (4)	170
N4—H4···O31	0.86	2.12	2.951 (3)	162
N5—H5C···O52	0.90	2.01	2.908 (3)	172
N5—H5D···O42	0.90	2.17	3.064 (4)	177
N6—H6···O21	0.86	2.30	3.096 (4)	154
N11—H11A···O31^{iii}	0.90	2.17	3.071 (3)	177
N11—H11B···O22	0.90	2.17	2.989 (3)	151
N12—H12···O51^{iii}	0.86	2.19	2.960 (3)	150
N13—H13D···O23	0.90	2.26	3.046 (4)	146
N13—H13E···O42	0.90	2.30	3.091 (4)	146
N14—H14···O53	0.86	2.25	2.984 (4)	143
N15—H15C···O32	0.90	2.20	3.077 (4)	165
N15—H15D···O41	0.90	2.10	2.951 (4)	157
N16—H16···O31^{iv}	0.86	2.13	2.962 (3)	163
N16—H16···O32^{iv}	0.86	2.40	3.113 (4)	141

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

Fig. 1


C19
C18
O16
O15
C17
C15
C16
C13
C12
O11
C11
N16
O13
N15
O14
O12
Ni2
C14
N12
N11
N14
N13