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Crystal structure of hexaaquanickel(II) bis{5-bromo-7-[(2-hydroxyethyl)amino]-1-methyl-6-oxidoquinolin-1-ium-3-sulfonate} monohydrate

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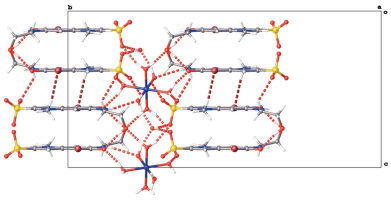
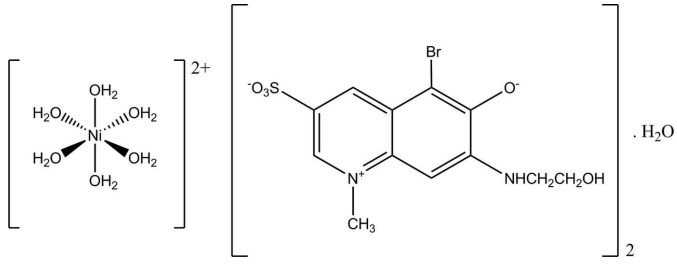
The asymmetric unit of the title compound, $[Ni(H_2O)_6](C_{12}H_{12}BrN_2O_5S)_2\cdot H_2O$, contains a half hexaaquanickel(II) complex cation with the Ni^{II} ion lying on an inversion center, one 5-bromo-7-[(2-hydroxyethyl)amino]-1-methyl-6-oxidoquinolin-1-ium-3-sulfonate (**QAO**) anion and a half lattice water molecule on a twofold rotation axis. In the crystal, **QAO** anions are stacked in a column along the *c* axis by π–π stacking interactions [centroid–centroid distances 3.5922 (10)–3.7223 (11) Å]. The columns are interlinked by hexaaquanickel(II) cations through O—H···O and N—H···O hydrogen bonds.

1. Chemical context

Among heterocyclic rings, the quinoline ring system is of great importance due to its therapeutic and biological activities. Many new quinoline derivatives have been synthesized and used as new potential agents to treat HIV (Cecchetti *et al.*, 2000; Tabarrini *et al.*, 2008) and malaria (Nayyar *et al.*, 2006) or to inhibit human tumor cell growth (Rashad *et al.*, 2010). Recently, a simple aminoquinoline derivative has been used in colorimetric sensors for pH (Wang *et al.*, 2014). In addition, complexes of quinoline compounds with transition metals are also known to exhibit a wide variety of structures and possess profound biochemical activities which allow them to act as antimicrobial, anti-Alzheimer's (Deraeve *et al.*, 2008) or antitumoral agents (Yan *et al.*, 2012; Kitanovic *et al.*, 2014). Some complexes of polysubstituted quinoline compounds have also been used in dye-sensitized solar cells or in efficient organic heterojunction solar cells (Li *et al.*, 2012).





The new quinoline derivative (6-hydroxy-3-sulfoquinolin-7-yloxy)acetic acid (**Q**) was synthesized from eugenol and its antibacterial activities have been reported (Dinh *et al.*, 2012). From **Q**, a series of polysubstituted quinoline compounds has

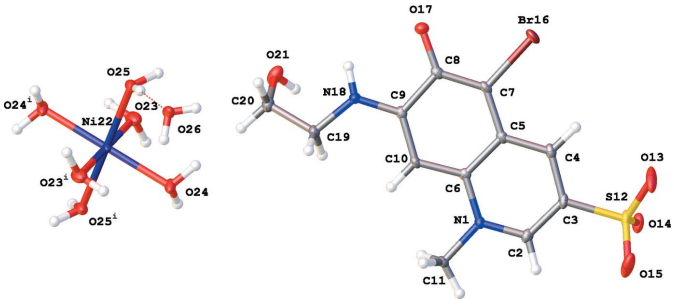


Figure 1
The structures of the molecular components in the title compound with ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x+\frac{1}{2}$, $-y+\frac{3}{2}$, $-z+1$.]

been synthesized, including 5-bromo-6-hydroxy-7-[(2-hydroxyethyl)amino]-1-methyl-3-sulfoquinoline (**QAO**). As polysubstituted quinoline rings are known to coordinate to metal ions, the reaction between **QAO** and $NiCl_2$ was studied. The reaction product could not be characterized unambiguously by IR or ^{1}H NMR spectroscopy. Although the obtained spectroscopic data are different from those of free **QAO**, indicating the presence of a deprotonated hydroxyl group, no conclusion about complex formation was possible and further investigation by X-ray diffraction was necessary.

2. Structural commentary

The structure determination shows that Ni^{II} is not complexed directly with **QAO**, but is present as a hexaaqua complex, $[Ni(H_2O)_6]^{2+}$, located about an inversion center (Fig. 1). The 6-hydroxy group as well as the 3-sulfonic acid group of **QAO** are deprotonated. The substituent atom Br16 deviates most [0.125 (1) Å] from the best plane through the quinoline ring system (r.m.s. deviation = 0.009 Å). The 2-hydroxyethylamino substituent shows a *+sc* conformation [torsion angle N18—C19—C20—O21 = 57.0 (2)°].

3. Supramolecular features

The crystal packing (Fig. 2) is characterized by columns of stacking **QAO** molecules running along the *c* axis through π–π stacking interactions between the quinoline ring systems

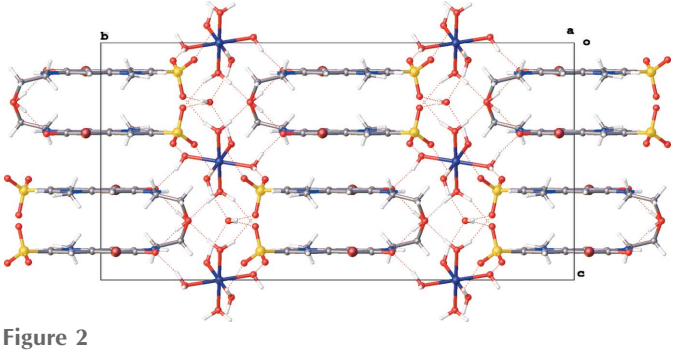


Figure 2
Packing diagram of the title compound viewed along the *a* axis. Dashed lines represent hydrogen bonds.

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

D—H···A	D—H	H···A	D···A	D—H···A
O21—H21···O17^{i}	0.83 (3)	1.89 (3)	2.707 (2)	170 (3)
C11—H11B···Br16^{ii}	0.98	3.02	3.987 (2)	171
C19—H19A···O13^{ii}	0.99	2.59	3.360 (3)	134
N18—H18···O25^{iii}	0.88	2.58	3.422 (2)	159
O23—H23A···O14^{iv}	0.92	2.09	2.971 (2)	161
O23—H23B···O21^{v}	0.91	1.72	2.630 (2)	172
O24—H24A···O13^{ii}	0.90	1.90	2.772 (2)	162
O24—H24B···O17^{vi}	0.90	1.83	2.714 (2)	165
O25—H25A···O15^{vii}	0.92	2.16	2.826 (2)	129
O25—H25B···O26	0.91	1.86	2.755 (2)	165
O26—H26···O14^{ii}	0.76 (3)	2.03 (3)	2.783 (2)	175 (3)

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

[$Cg1\cdots Cg1^{i}$ = 3.5922 (10) Å, $Cg2\cdots Cg2^{i}$ = 3.5793 (11) Å, $Cg1\cdots Cg2^{ii}$ = 3.7223 (11) Å; $Cg1$ and $Cg2$ are the centroids of the rings N1/C2–C6 and C5–C10, respectively; symmetry codes: (i) $-x+2, y, -z+\frac{1}{2}$; (ii) $-x+2, -y+1, -z+1$; Fig. 3]. Within these columns additional C—H···Br and C—H···O interactions occur (Table 1 and Fig. 3). The columns interact with the hexaaquanickel(II) cations through hydrogen bonding. The lattice water molecule interacts with two neighboring cations. One $[Ni(H_2O)_6]^{2+}$ complex interacts in total with twelve **QAO** molecules and two water molecules through O—H···O and N—H···O hydrogen bonds (Table 1 and Fig. 4).

4. Database survey

A search of the Cambridge Structural Database (Version 5.37; last update May 2016; Groom *et al.*, 2016) for 3-quinolinium sulfonic acids gives six hits of which four have a zwitterionic form [CSD refcodes PUSMOH (Le Thi Hong *et al.*, 2015), BAPBOK (Skrzypek & Suwinska, 2002), HIVHUQ (Skrzypek & Suwinska, 2007) and QUNREY (Dinh *et al.*,

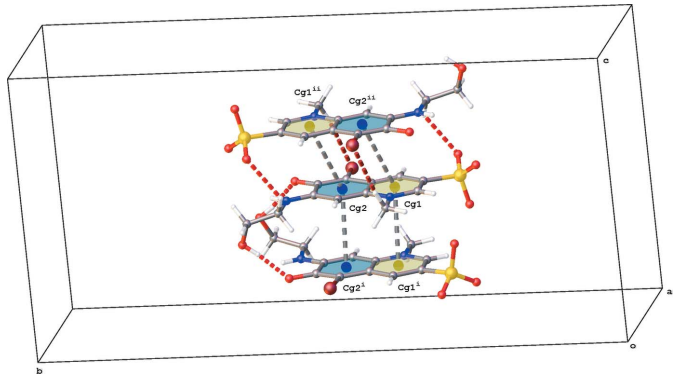


Figure 3
Partial packing diagram of the title compound, showing π–π interactions between quinoline ring systems [grey dotted lines; $Cg1$ and $Cg2$ are the centroids of rings N1/C2–C6 and C5–C10, respectively; symmetry codes: (i) $-x+2, y, -z+\frac{1}{2}$; (ii) $-x+2, -y+1, -z+1$], and C—H···Br and C—H···O hydrogen bonds (red dotted lines).

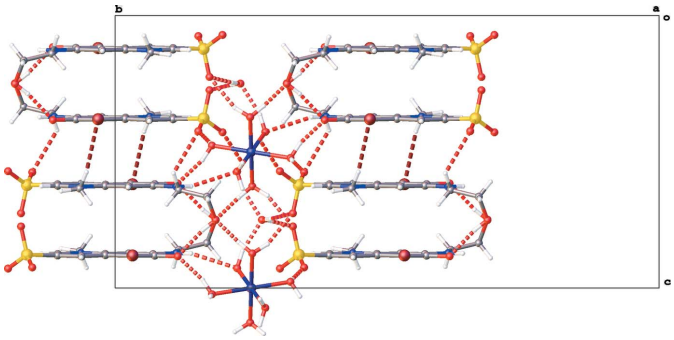


Figure 4
Partial packing diagram of the title compound viewed along the *a* axis, showing the *X*—H···O hydrogen bonds (red dotted lines, see Table 1 for details) and C—H···Br interactions (brown dotted lines).

2012)]. The remaining two are *N*-methylated [CSD refcode HIVJEC (Skrzypek & Suwinska, 2007)] or *N*-ethylated [CSD refcode HIVJAY (Skrzypek & Suwinska, 2007)] and have a hydroxyl group at the 4-position.

5. Synthesis and crystallization

The quinoline derivative (6-hydroxy-3-sulfoquinolin-7-yloxy)-acetic acid (**Q**) was synthesized starting from the natural product eugenol and further transformed to 5-bromo-6-hydroxy-7-[(2-hydroxyethyl)amino]-1-methyl-3-sulfoquinoline (**QAO**) according to a procedure described by Dinh *et al.* (2012).

A solution containing $NiCl_2{\cdot}6H_2O$ (262 mg, 1.1 mmol) in 10 mL water was added dropwise to 15 mL aqueous solution of **QAO** (754 mg, 2 mmol) and NH_3 (pH $\simeq$ 6–7). The obtained solution was stirred and refluxed at 313–323 K for three h. The brown precipitate was collected by filtration, washed consecutively with ethanol and dried *in vacuo*. The obtained crystals were soluble in water and DMSO, but insoluble in ethanol, acetone and chloroform. The yield was 60%. Single crystals suitable for X-ray investigation were obtained by slow evaporation from a ethanol–water (1:2 *v*/*v*) solution at room temperature.

IR (Impack-410 Nicolet spectrometer, KBr, cm^{-1}): 3510, 3334 (ν_{NH}, ν_{OH}); 3080, 2942 ($\nu_{C\text{-}H}$); 1588, 1540 ($\nu_{C=Cring}$ or $\nu_{C=N}$); 1190, 1036 ($\nu_{C\text{-}O}$, $\nu_{S\text{-}O}$), 632 ($\nu_{C\text{-}Br}$). ^{1}H NMR (Bruker Avance 500 MHz, d_6-DMSO): 8.34 (1H, *d*, *J* =1.0Hz, Ar), 8.27 (1H, *s*, Ar), 6.51 (1H, *s*, Ar), 4.22 (3H, *s*, N-CH3); 3.69 (2H, *t*, *J* = 5.5Hz); 3.45 (2H, *q*, *J* = 5.5Hz), 7.34 (NH).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms for N18, O21, O23, O24, O25 and O26 were located in difference Fourier maps. The coordinates of H21 and H26 were refined freely, while the other H atoms were refined as riding. All C-bound H atoms were placed at idealized positions and refined as riding, with C—H distances of 0.95 (aromatic), 0.99 (methylene) and 0.98 Å (methyl). For most H atoms, U_{iso}(H) values were assigned as 1.5U_{eq} of the parent atoms (1.2U_{eq} for H2, H4, H10, H18, H19*A*/*B* and H20*A*/*B*).

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ni(H_2O)_6](C_{12}H_{12}BrN_2O_5S)_2{\cdot}H_2O$
M_r	937.23
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	100
a, *b*, *c* (Å)	8.7315 (4), 27.4581 (13), 13.7943 (6)
β (°)	94.061 (4)
V (Å^3)	3298.9 (3)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	3.22
Crystal size (mm)	0.4 × 0.2 × 0.1
Data collection	
Diffractometer	Agilent SuperNova (single source at offset, Eos detector)
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015)
T_{min}, T_{max}	0.546, 0.725
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9171, 3372, 3041
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.024, 0.056, 1.08
No. of reflections	3372
No. of parameters	235
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.49

Computer programs: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

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References

Cecchetti, V., Parolin, C., Moro, S., Pecere, T., Filipponi, E., Calistri, A., Tabarrini, O., Gatto, B., Palumbo, M., Fravolini, A. & Palu', G. (2000). *J. Med. Chem.* **43**, 3799–3802.
Deraeve, C., Boldron, C., Maraval, A., Mazarguil, H., Gornitzka, H., Vendier, L., Pitié, M. & Meunier, B. (2008). *Chem. Eur. J.* **14**, 682–696.
Dinh, N. H., Co, L. V., Tuan, N. M., Hai, L. T. H. & Van Meervelt, L. (2012). *Heterocycles*, **85**, 627–637.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Kitanovic, I., Can, S., Alborzinia, H., Kitanovic, A., Pierroz, V., Leonidova, A., Pinto, A., Spingler, B., Ferrari, S., Molteni, R., Steffen, A., Metzler-Nolte, N., Wölfl, S. & Gasser, G. (2014). *Chem. Eur. J.* **20**, 2496–2507.

Le Thi Hong, H., Nguyen Thi Ngoc, V., Tran Thi, D., Nguyen Bich, N. & Van Meervelt, L. (2015). *Acta Cryst.* E**71**, 1105–1108.
Li, J.-Y., Chen, C.-Y., Ho, W.-C., Chen, S.-H. & Wu, C.-G. (2012). *Org. Lett.* **14**, 5420–5423.
Nayyar, A., Malde, A., Coutinho, E. & Jain, R. (2006). *Bioorg. Med. Chem.* **14**, 7302–7310.
Rashad, A. E., El-Sayed, W. A., Mohamed, A. M. & Ali, M. M. (2010). *Arch. Pharm. Pharm. Med. Chem.* **343**, 440–448.
Rigaku Oxford Diffraction (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Skrzypek, L. & Suwinska, K. (2002). *Heterocycles*, **57**, 2035–2044.
Skrzypek, L. & Suwinska, K. (2007). *Heterocycles*, **71**, 1363–1370.
Tabarrini, O., Massari, S., Daelemans, D., Stevens, M., Manfroni, G., Sabatini, S., Balzarini, J., Cecchetti, V., Pannecouque, C. & Fravolini, A. (2008). *J. Med. Chem.* **51**, 5454–5458.
Wang, Q., Li, R., Qui, S., Lin, Z., Chen, G. & Luo, L. (2014). *Anal. Methods*, **6**, 5016–5019.
Yan, L., Wang, X., Wang, Y., Zhang, Y., Li, Y. & Guo, Z. (2012). *J. Inorg. Biochem.* **106**, 46–51.

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Computing details

Data collection: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015); cell refinement: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015); data reduction: *CrysAlis PRO* (Rigaku Oxford Diffraction, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Hexaaquanickel(II) bis{5-bromo-7-[(2-hydroxyethyl)amino]-1-methyl-6-oxidoquinoline-1-ium-3-sulfonate} monohydrate

Crystal data

$[Ni(H_2O)_6](C_{12}H_{12}BrN_2O_5S)_2\cdot H_2O$
$M_r = 937.23$
Monoclinic, $C2/c$
$a = 8.7315$ (4) Å
$b = 27.4581$ (13) Å
$c = 13.7943$ (6) Å
$\beta = 94.061$ (4)°
$V = 3298.9$ (3) Å^3
$Z = 4$
$F(000) = 1904$
$D_x = 1.887$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5359 reflections
$\theta = 2.8$–$29.0°$
$\mu = 3.22$ mm^{-1}
$T = 100$ K
Plate, orange
0.4 × 0.2 × 0.1 mm

Data collection

Agilent SuperNova (single source at offset, Eos detector) diffractometer
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 15.9631 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Rigaku Oxford Diffraction, 2015)
$T_{min} = 0.546$, $T_{max} = 0.725$
9171 measured reflections
3372 independent reflections
3041 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 26.4°$, $\theta_{min} = 2.5°$
$h = -10\rightarrow10$
$k = -34\rightarrow32$
$l = -12\rightarrow17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.056$
$S = 1.08$
3372 reflections
235 parameters
0 restraints

Primary atom site location: structure-invariant direct methods	$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 5.2045P]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: mixed	$(\Delta/\sigma)_{max} = 0.002$
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{max} = 0.41$ e Å^{-3}
	$\Delta\rho_{min} = -0.49$ 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}
N1	0.90237 (18)	0.43668 (6)	0.37155 (11)	0.0110 (3)
C2	0.9801 (2)	0.39411 (8)	0.37514 (14)	0.0132 (4)
H2	0.9254	0.3642	0.3739	0.016*
C3	1.1379 (2)	0.39384 (8)	0.38056 (14)	0.0131 (4)
C4	1.2182 (2)	0.43770 (8)	0.38321 (13)	0.0134 (4)
H4	1.3273	0.4374	0.3877	0.016*
C5	1.1403 (2)	0.48189 (8)	0.37930 (13)	0.0108 (4)
C6	0.9750 (2)	0.48132 (8)	0.37471 (13)	0.0104 (4)
C7	1.2125 (2)	0.52820 (8)	0.38177 (14)	0.0119 (4)
C8	1.1373 (2)	0.57248 (8)	0.38109 (13)	0.0122 (4)
C9	0.9683 (2)	0.56934 (8)	0.37556 (13)	0.0110 (4)
C10	0.8918 (2)	0.52466 (8)	0.37301 (13)	0.0113 (4)
H10	0.7828	0.5238	0.3701	0.014*
C11	0.7332 (2)	0.43449 (8)	0.36504 (14)	0.0128 (4)
H11A	0.6923	0.4543	0.3101	0.019*
H11B	0.6950	0.4470	0.4253	0.019*
H11C	0.6999	0.4006	0.3553	0.019*
S12	1.23734 (6)	0.33760 (2)	0.37750 (4)	0.01589 (12)
O13	1.3871 (2)	0.34725 (7)	0.42443 (13)	0.0360 (5)
O14	1.24175 (17)	0.32666 (6)	0.27422 (10)	0.0200 (3)
O15	1.1481 (2)	0.30278 (6)	0.42858 (12)	0.0323 (4)
Br16	1.42949 (2)	0.53172 (2)	0.38060 (2)	0.01722 (7)
O17	1.19947 (16)	0.61482 (5)	0.38363 (10)	0.0154 (3)
N18	0.89569 (19)	0.61215 (7)	0.37205 (12)	0.0136 (4)
H18	0.9506	0.6391	0.3730	0.016*
C19	0.7298 (2)	0.61683 (8)	0.35993 (15)	0.0139 (4)
H19A	0.6846	0.6070	0.4208	0.017*
H19B	0.6892	0.5947	0.3075	0.017*
C20	0.6831 (2)	0.66848 (8)	0.33499 (15)	0.0162 (4)
H20A	0.5699	0.6704	0.3248	0.019*
H20B	0.7159	0.6902	0.3899	0.019*
O21	0.75070 (19)	0.68455 (6)	0.24924 (11)	0.0229 (4)
H21	0.760 (3)	0.6610 (11)	0.213 (2)	0.034*
Ni22	0.2500	0.7500	0.5000	0.01747 (10)

O23	0.35588 (18)	0.75193 (6)	0.37316 (12)	0.0273 (4)
H23A	0.3304	0.7799	0.3392	0.041*
H23B	0.3270	0.7270	0.3322	0.041*
O24	0.31091 (17)	0.67782 (6)	0.52289 (12)	0.0237 (4)
H24A	0.4136	0.6748	0.5315	0.036*
H24B	0.2816	0.6604	0.4695	0.036*
O25	0.44976 (16)	0.77588 (5)	0.57273 (12)	0.0196 (3)
H25A	0.5337	0.7662	0.5414	0.029*
H25B	0.4680	0.7661	0.6357	0.029*
O26	0.5000	0.73024 (9)	0.7500	0.0218 (5)
H26	0.570 (3)	0.7142 (10)	0.746 (2)	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0109 (8)	0.0116 (9)	0.0102 (8)	0.0017 (7)	0.0001 (6)	−0.0009 (7)
C2	0.0169 (10)	0.0120 (10)	0.0106 (9)	0.0023 (8)	−0.0005 (8)	0.0001 (8)
C3	0.0151 (10)	0.0137 (11)	0.0102 (9)	0.0061 (8)	0.0001 (7)	−0.0021 (8)
C4	0.0125 (10)	0.0178 (11)	0.0098 (9)	0.0049 (8)	0.0007 (7)	−0.0004 (8)
C5	0.0103 (9)	0.0153 (11)	0.0070 (8)	0.0009 (8)	0.0010 (7)	−0.0001 (8)
C6	0.0118 (9)	0.0132 (11)	0.0064 (8)	−0.0002 (8)	0.0014 (7)	−0.0001 (8)
C7	0.0075 (9)	0.0184 (11)	0.0099 (9)	0.0003 (8)	0.0009 (7)	0.0005 (8)
C8	0.0109 (10)	0.0178 (11)	0.0078 (9)	−0.0010 (8)	0.0003 (7)	0.0001 (8)
C9	0.0111 (10)	0.0142 (11)	0.0077 (9)	0.0018 (8)	0.0003 (7)	−0.0011 (8)
C10	0.0079 (9)	0.0150 (11)	0.0111 (9)	0.0017 (8)	0.0007 (7)	0.0001 (8)
C11	0.0079 (9)	0.0140 (11)	0.0166 (10)	0.0003 (8)	0.0005 (7)	0.0003 (8)
S12	0.0176 (3)	0.0156 (3)	0.0141 (2)	0.0096 (2)	−0.00095 (19)	−0.0023 (2)
O13	0.0268 (9)	0.0349 (11)	0.0431 (11)	0.0212 (8)	−0.0198 (8)	−0.0210 (9)
O14	0.0243 (8)	0.0199 (9)	0.0156 (7)	0.0105 (7)	0.0008 (6)	−0.0038 (6)
O15	0.0481 (11)	0.0194 (9)	0.0315 (9)	0.0170 (8)	0.0186 (8)	0.0112 (8)
Br16	0.00740 (10)	0.02418 (13)	0.02029 (11)	0.00080 (8)	0.00253 (7)	0.00294 (9)
O17	0.0144 (7)	0.0140 (8)	0.0177 (7)	−0.0023 (6)	−0.0002 (6)	0.0003 (6)
N18	0.0113 (8)	0.0107 (9)	0.0189 (9)	−0.0004 (7)	0.0006 (7)	0.0002 (7)
C19	0.0094 (10)	0.0138 (11)	0.0184 (10)	0.0013 (8)	0.0001 (8)	0.0003 (9)
C20	0.0162 (10)	0.0160 (11)	0.0163 (10)	0.0034 (9)	−0.0004 (8)	−0.0003 (9)
O21	0.0355 (9)	0.0159 (9)	0.0179 (8)	0.0045 (7)	0.0053 (7)	0.0017 (7)
Ni22	0.00750 (18)	0.0097 (2)	0.0349 (2)	−0.00015 (14)	−0.00080 (16)	−0.00713 (17)
O23	0.0182 (8)	0.0217 (9)	0.0422 (10)	−0.0036 (7)	0.0036 (7)	−0.0123 (8)
O24	0.0136 (7)	0.0140 (8)	0.0422 (10)	0.0032 (6)	−0.0073 (7)	−0.0106 (7)
O25	0.0107 (7)	0.0148 (8)	0.0331 (9)	−0.0003 (6)	0.0004 (6)	−0.0042 (7)
O26	0.0133 (11)	0.0133 (12)	0.0403 (14)	0.000	0.0117 (10)	0.000

Geometric parameters (Å, º)

N1—C2	1.351 (3)	S12—O15	1.4474 (18)
N1—C6	1.380 (3)	N18—H18	0.8806
N1—C11	1.475 (2)	N18—C19	1.452 (2)
C2—H2	0.9500	C19—H19A	0.9900

C2—C3	1.374 (3)	C19—H19B	0.9900
C3—C4	1.393 (3)	C19—C20	1.509 (3)
C3—S12	1.774 (2)	C20—H20A	0.9900
C4—H4	0.9500	C20—H20B	0.9900
C4—C5	1.390 (3)	C20—O21	1.429 (3)
C5—C6	1.440 (3)	O21—H21	0.83 (3)
C5—C7	1.418 (3)	Ni22—O23^{i}	2.0366 (17)
C6—C10	1.394 (3)	Ni22—O23	2.0366 (17)
C7—C8	1.381 (3)	Ni22—O24	2.0704 (15)
C7—Br16	1.8983 (19)	Ni22—O24^{i}	2.0704 (15)
C8—C9	1.474 (3)	Ni22—O25	2.0750 (14)
C8—O17	1.283 (3)	Ni22—O25^{i}	2.0750 (14)
C9—C10	1.397 (3)	O23—H23A	0.9191
C9—N18	1.335 (3)	O23—H23B	0.9115
C10—H10	0.9500	O24—H24A	0.9003
C11—H11A	0.9800	O24—H24B	0.9001
C11—H11B	0.9800	O25—H25A	0.9163
C11—H11C	0.9800	O25—H25B	0.9128
S12—O13	1.4420 (17)	O26—H26	0.76 (3)
S12—O14	1.4592 (15)		

C2—N1—C6	122.61 (17)	O15—S12—O14	113.06 (10)
C2—N1—C11	117.74 (18)	C9—N18—H18	118.8
C6—N1—C11	119.64 (17)	C9—N18—C19	123.35 (18)
N1—C2—H2	119.8	C19—N18—H18	117.7
N1—C2—C3	120.4 (2)	N18—C19—H19A	109.4
C3—C2—H2	119.8	N18—C19—H19B	109.4
C2—C3—C4	119.84 (19)	N18—C19—C20	111.15 (17)
C2—C3—S12	119.61 (17)	H19A—C19—H19B	108.0
C4—C3—S12	120.46 (15)	C20—C19—H19A	109.4
C3—C4—H4	119.7	C20—C19—H19B	109.4
C5—C4—C3	120.66 (19)	C19—C20—H20A	109.4
C5—C4—H4	119.7	C19—C20—H20B	109.4
C4—C5—C6	118.55 (19)	H20A—C20—H20B	108.0
C4—C5—C7	124.51 (18)	O21—C20—C19	111.00 (17)
C7—C5—C6	116.92 (18)	O21—C20—H20A	109.4
N1—C6—C5	117.92 (18)	O21—C20—H20B	109.4
N1—C6—C10	121.32 (18)	C20—O21—H21	109 (2)
C10—C6—C5	120.76 (19)	O23^{i}—Ni22—O23	180.00 (4)
C5—C7—Br16	119.16 (15)	O23^{i}—Ni22—O24	88.36 (7)
C8—C7—C5	125.37 (18)	O23—Ni22—O24^{i}	88.36 (7)
C8—C7—Br16	115.42 (15)	O23—Ni22—O24	91.64 (7)
C7—C8—C9	114.98 (19)	O23^{i}—Ni22—O24^{i}	91.64 (7)
O17—C8—C7	126.71 (18)	O23^{i}—Ni22—O25^{i}	89.39 (6)
O17—C8—C9	118.31 (18)	O23—Ni22—O25	89.39 (6)
C10—C9—C8	121.87 (19)	O23^{i}—Ni22—O25	90.61 (6)
N18—C9—C8	114.94 (18)	O23—Ni22—O25^{i}	90.61 (6)
N18—C9—C10	123.18 (18)	O24—Ni22—O24^{i}	180.0

C6—C10—C9	120.10 (18)	O24^{i}—Ni22—O25	86.79 (6)
C6—C10—H10	120.0	O24—Ni22—O25	93.21 (6)
C9—C10—H10	120.0	O24—Ni22—O25^{i}	86.79 (6)
N1—C11—H11A	109.5	O24^{i}—Ni22—O25^{i}	93.21 (6)
N1—C11—H11B	109.5	O25^{i}—Ni22—O25	180.0
N1—C11—H11C	109.5	Ni22—O23—H23A	110.6
H11A—C11—H11B	109.5	Ni22—O23—H23B	113.0
H11A—C11—H11C	109.5	H23A—O23—H23B	105.3
H11B—C11—H11C	109.5	Ni22—O24—H24A	110.6
O13—S12—C3	105.03 (10)	Ni22—O24—H24B	109.2
O13—S12—O14	112.98 (10)	H24A—O24—H24B	106.3
O13—S12—O15	113.89 (12)	Ni22—O25—H25A	110.3
O14—S12—C3	104.43 (9)	Ni22—O25—H25B	116.3
O15—S12—C3	106.39 (10)	H25A—O25—H25B	105.9

N1—C2—C3—C4	0.5 (3)	C6—N1—C2—C3	−1.1 (3)
N1—C2—C3—S12	−176.06 (14)	C6—C5—C7—C8	0.7 (3)
N1—C6—C10—C9	−179.52 (17)	C6—C5—C7—Br16	−176.56 (13)
C2—N1—C6—C5	1.8 (3)	C7—C5—C6—N1	179.55 (16)
C2—N1—C6—C10	−178.59 (17)	C7—C5—C6—C10	−0.1 (3)
C2—C3—C4—C5	−0.7 (3)	C7—C8—C9—C10	1.1 (3)
C2—C3—S12—O13	−156.31 (17)	C7—C8—C9—N18	−178.14 (17)
C2—C3—S12—O14	84.58 (17)	C8—C9—C10—C6	−0.6 (3)
C2—C3—S12—O15	−35.24 (19)	C8—C9—N18—C19	175.77 (17)
C3—C4—C5—C6	1.4 (3)	C9—N18—C19—C20	−166.55 (18)
C3—C4—C5—C7	179.87 (18)	C10—C9—N18—C19	−3.5 (3)
C4—C3—S12—O13	27.10 (19)	C11—N1—C2—C3	179.54 (17)
C4—C3—S12—O14	−92.01 (17)	C11—N1—C6—C5	−178.90 (16)
C4—C3—S12—O15	148.17 (17)	C11—N1—C6—C10	0.8 (3)
C4—C5—C6—N1	−1.9 (3)	S12—C3—C4—C5	175.84 (14)
C4—C5—C6—C10	178.47 (17)	Br16—C7—C8—C9	176.19 (13)
C4—C5—C7—C8	−177.81 (18)	Br16—C7—C8—O17	−3.0 (3)
C4—C5—C7—Br16	5.0 (3)	O17—C8—C9—C10	−179.67 (17)
C5—C6—C10—C9	0.1 (3)	O17—C8—C9—N18	1.1 (3)
C5—C7—C8—C9	−1.1 (3)	N18—C9—C10—C6	178.53 (17)
C5—C7—C8—O17	179.72 (18)	N18—C19—C20—O21	57.0 (2)

Symmetry code: (i) −*x*+1/2, −*y*+3/2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21—H21···O17^{ii}	0.83 (3)	1.89 (3)	2.707 (2)	170 (3)
C11—H11*B*···Br16^{iii}	0.98	3.02	3.987 (2)	171
C19—H19*A*···O13^{iii}	0.99	2.59	3.360 (3)	134
N18—H18···O25^{iv}	0.88	2.58	3.422 (2)	159
O23—H23*A*···O14^{v}	0.92	2.09	2.971 (2)	161
O23—H23*B*···O21^{vi}	0.91	1.72	2.630 (2)	172

O24—H24*A*···O13^{iii}	0.90	1.90	2.772 (2)	162
O24—H24*B*···O17^{vii}	0.90	1.83	2.714 (2)	165
O25—H25*A*···O15^{viii}	0.92	2.16	2.826 (2)	129
O25—H25*B*···O26	0.91	1.86	2.755 (2)	165
O26—H26···O14^{iii}	0.76 (3)	2.03 (3)	2.783 (2)	175 (3)

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