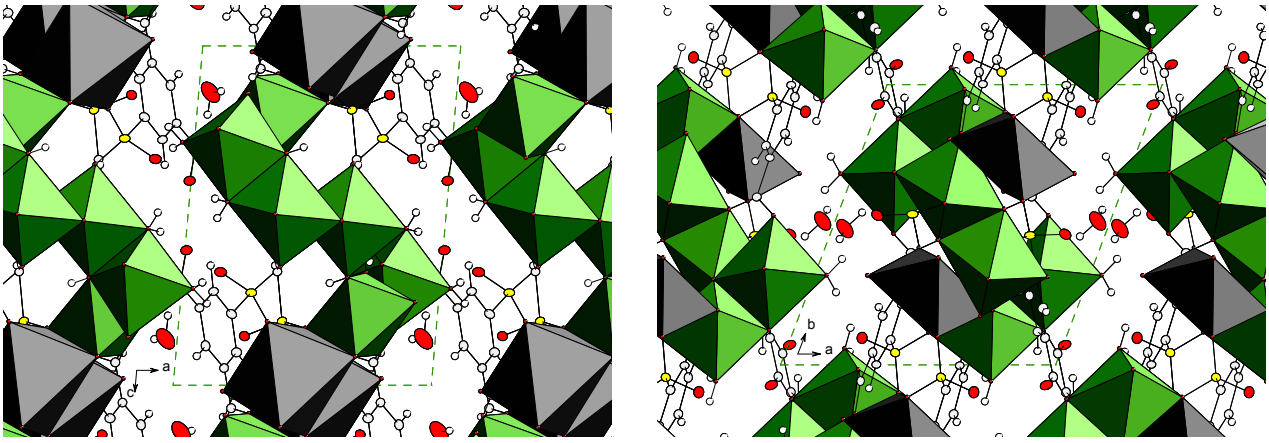
Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Material

Structure description:

The structure of **1** may be described as clusters of six NiO_6 and two NaO_6 octahedra bridged into a three-dimensional coordination polymer through SIPA as shown in Figure 1. S letter-shaped cavities running along the *c*-axis contain several coordinated water molecules (O1w, O3w, O4w) directed towards a cavity as well as an uncoordinated water molecule (O6w).



(a) (b)

Fig. 1 Several unit cells of **1**, displaying pores with crystallographic water molecules along the b (a) and c (b) axis, respectively. Nickel and sodium atoms are represented as green and dark grey octahedra, oxygen and sulfur atoms as red and yellow, and carbon and hydrogen atoms as large and small, light grey, respectively.

The six-nickel cluster presented in **1** is new, containing three crystallographically independent nickel atoms joined by one unique μ_3-OH (O1h) (Fig. 2a). An inversion center occurs along an edge-sharing connection at the center of the cluster. The octahedral environment around the Ni(1) atom consists of three carboxylate oxygen atoms, two coordinated water molecules, and one μ_3-hydroxide. Ni(2) and Ni(3) are surrounded by three carboxylate and one sulfonate oxygen atoms, one water molecule and one μ_3-hydroxide. The bond distances and angles of three Ni atoms, presented in Table 3, are typical for octahedral Ni(II). The single unique sodium atom Na(1), is surrounded by a distorted octahedron of one carboxylate and three sulfonate oxygen atoms, as well as two terminal water molecules (O4w, O5w). The octahedra surrounding

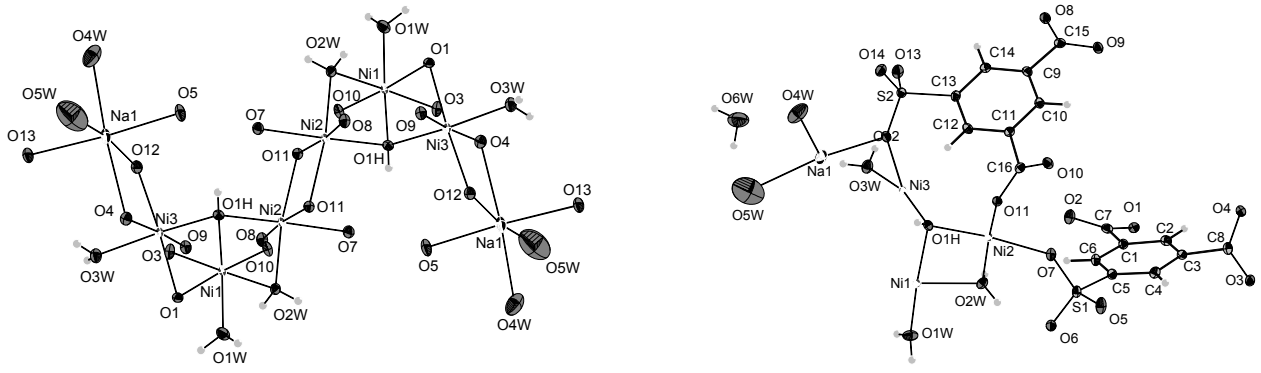
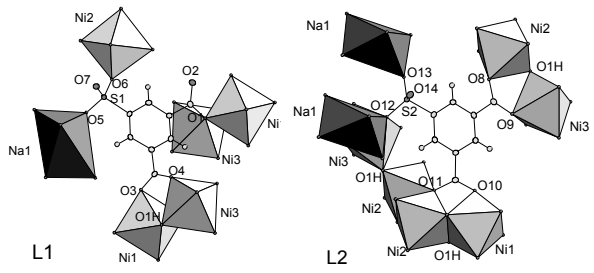


Fig. 2 (a) The $Na_2Ni_6O_{36}$ cluster present in **1**, (b) asymmetric unit of **1**.

the sodium atoms are distorted, with O-Na-O angles ranging from 67.25(7)° to 117.56(9), and bond lengths ranging from 2.326(2) to 2.754(4) Å. The water molecules coordinating to the Na cation show large thermal parameters (Figure 2). The water molecule that does not participate in a hydrogen bond (O5W) shows a substantially larger thermal parameter than the one that does (O4W). Several clusters with related connectivity have been reported for $Ti_3(\mu 3\text{-}O)(O_2CH)_2(ONep)_8$ and $Ti_3(\mu 3\text{-}O)(O_2CMe)_2(ONep)_8$, which display corner-removed, inversion related, oxide-bridge cube and edge-shared cube, respectively,[i] as well as for $Hf_6O_2(OEt)_{20}(EtOH)_2$ comprising a four-membered $[Hf_2O_2]$ ring.[ii]



(b)

Fig. 3 the first ligand (L1) and the second ligand (L2) among of two distinct SIPA anions in **1**. Nickel and sodium atoms are represented in dark grey, oxygen and sulfur atoms as medium grey, and carbon and hydrogen atoms as large and small, light grey, respectively.

Figure 3 shows how two crystallographically SIPA anions (L1 and L2) coordinate to metal centers. Two sulfonate and one carboxylate oxygen atoms on these two ligands do not coordinate to a metal center, but participate in hydrogen bonding with coordinated and unbound water molecules in this compound. (O1w) possesses slightly weak H-bonds (O-O distances: 2.806 Å, 2.814 Å). Both occur with oxygen atoms (O14, O6) from the sulfonate groups in L1 and L2 that do not coordinate to a nickel center, as displayed in

Fig. 2b. The second bridging water molecule (O2w) has a particularly short as well as a more typical H-bond (2.498 Å, 2.719 Å) to additional uncoordinated oxygen atoms (O2 from carboxylate, O6 from sulfonate) from L1. Given the high acidity of protons on a μ_2 water molecule and the relative basicity of terminal carboxylate oxygen atoms, it is reasonable to expect a very strong hydrogen bond, explaining the short O-O distance. Similar hydrogen bonding between terminal carboxylate oxygen atom and bridging water molecules has been noted in an open framework cobalt 1,3,5-cyclohexanecarboxylate[iii] and open-framework nickel cyclopropionate containing an 18-membered ring.[iv]

In the terminal water molecules coordinated in Na octahedra, the fourth water molecule (O4w) appears to have a general H bond (2.736 Å) to a adjacent water oxygen atom (O3w) bound to Ni(3), while (O5w) is not involved in any hydrogen bonding. The Na-O distance between O4w and O5w is substantially different (2.396(3) Å vs 2.754(4) Å). Presumably the hydrogen bonding interaction of O4w results in a partial negative charge leading to a much shorter bond. Unfortunately, we were unable to locate the H atoms involved in these hydrogen bonds. A free water molecule (Ow6) connects to the framework through hydrogen bonds (2.709 Å and 2.752 Å, respectively), to the coordinated water molecule (O4w) in Na(1), and to the coordinated O3 atom in Ni(1).

Variable temperature XRD.

Variable-temperature x-ray powder diffraction data were collected under vacuum on **1** using a Bruker D8 equipped with a position sensitive detector, Cu Kα radiation, and an Anton-Parr high temperature stage. Data were collected over the angular range of 6˚-31˚ 2θ from room temperature to 700 ˚C at increments of 20 ˚C. Because of complex changes between 300 - 400 ˚C, data were collected every 10 ˚C in this range. Figure 4 summarizes the diffraction results.

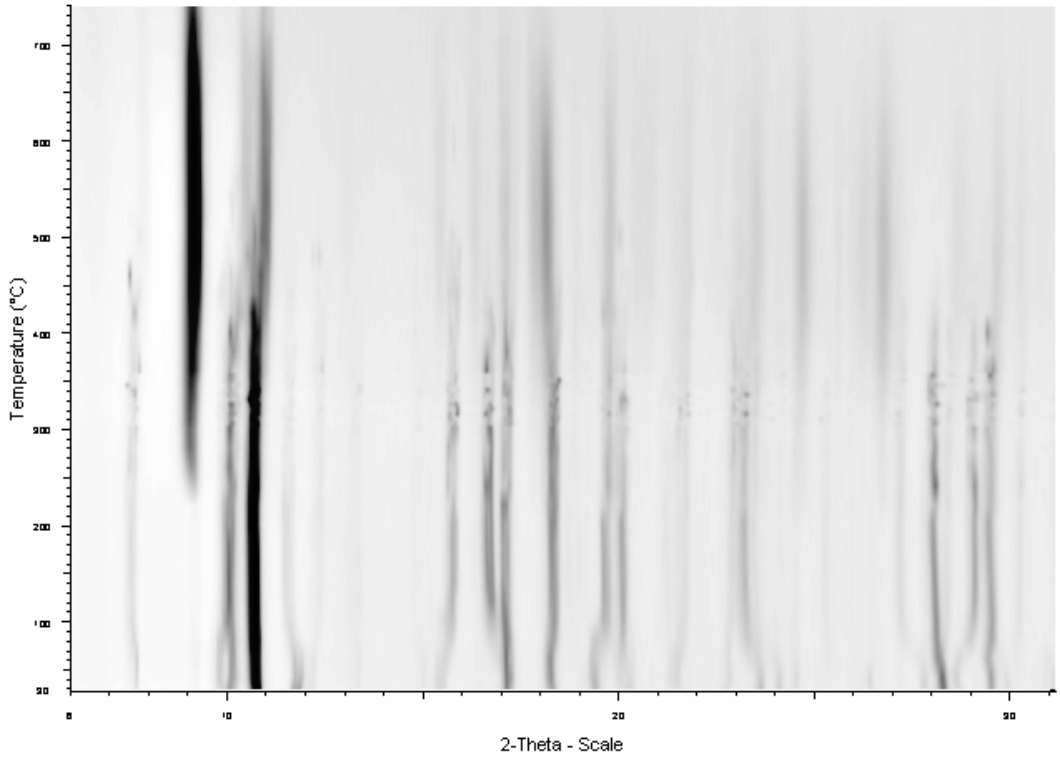


Fig. 4 (a) 2D plot of XRD diffraction data as a function of temperature for **1**. Darker regions indicate higher peak intensity. The onset of a very strong peak, beginning at about 250 ˚C, appears to coincide with the onset of porosity.

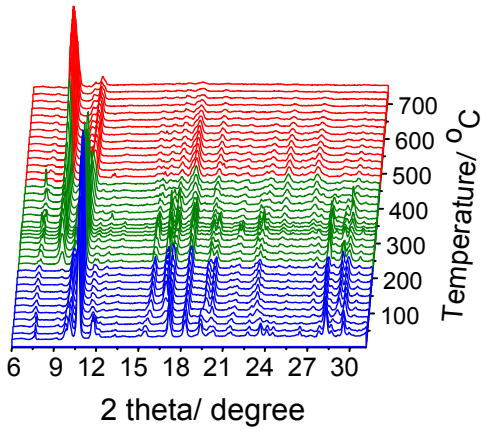


Fig. 4 (b) Pseudo 3d plot of XRD diffraction data as a function of temperature for **1**. The blue, green, and red regions indicate three major steps in the dehydration: a non-porous phase, a porous phase, and decomposion.

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Powder diffraction of dehydrated phase:

A powder diffraction pattern of the dehydrated phase was collected by dehydrating a sample at 300 ˚C overnight and loading the sample inside a solvent-free Ar glove box into a Be covered sample holder. A diffraction pattern was collected using a Scintag X2 powder diffractometer equipped with Cu Kα radiation (Figure 6). Figures 5 and 6 show the powder diffraction pattern for the dehydrated phase at room temperature. The powder diffraction pattern was indexed using DICVOL[1] by manually fitting 16 peaks. One unique cell was returned, which corresponded closely to the unit cell determined from single crystal diffraction.

[1] A. Boultif, D. Louër, *J. Appl. Cryst.* 1991, **24**, 987.

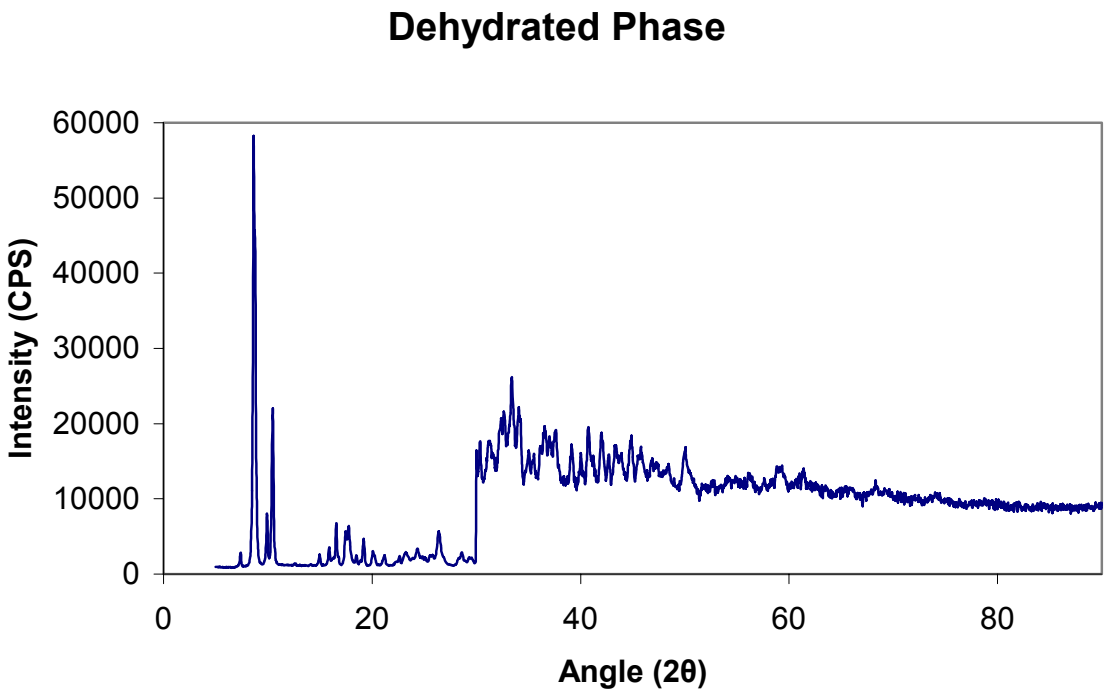

Fig. 5 (a) Plot of XRD powder diffraction data for the dehydrated phase of **1**. Data at angles larger than 30 ° is magnified by 10x for clarity.

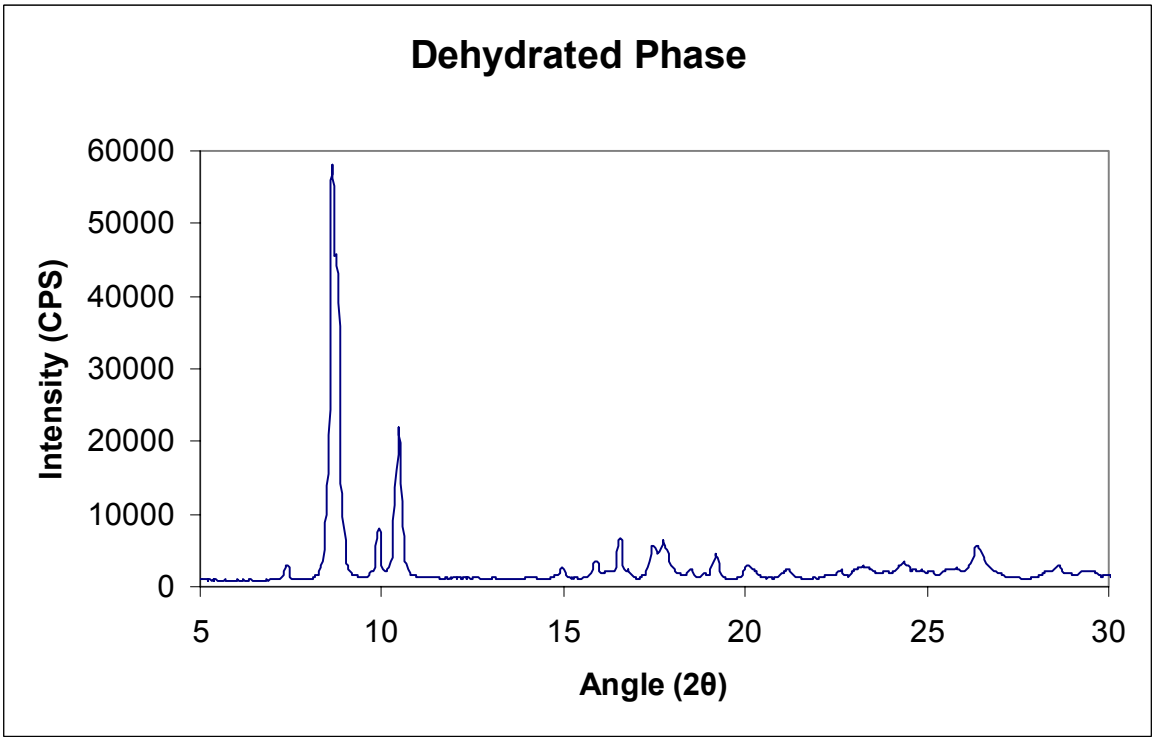

Fig. 6 (a) Plot of XRD powder diffraction data for the dehydrated phase of **1** from 5-30˚ 2θ.

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BET analysis:

Single Point Surface Area at P/P_o 0.10202576 :	743.1238 m^2/g
BET Surface Area :	750.1896 m^2/g
Langmuir Surface Area :	842.2374 m^2/g
Micropore Area:	722.8398 m^2/g
External Surface Area:	27.3499 m^2/g
Micropore Volume :	0.284052 cm^3/g

BET measurements were conducted on a Micromeritics ASAP 2000 with N_2 as the sorptive gas. This sample was prepared by overnight dehydration at 300 °C.

Crystallographic analysis:

Single-crystal diffraction data were collected using a Bruker SMART CCD system with MoK_α radiation (0.71073 Å). Because an attempt to solve the structure using direct methods did not generate a reasonable starting model, the structure was solved using the Patterson method and refined against $|F^2|$ using the SHELX-TL suite.[2] For this compound, hydrogen atoms were placed on the acid molecules using the riding model. In the case of the four water molecules in **1**, H atoms were located in the Fourier map and refined with isotropic temperature factors equal to 1.2 times that of the oxygen they were bonded to. Because some O-H distances refined to unreasonable values, all O-H distances were restrained to be equal to 0.80 Å within a standard deviation of 0.02 Å. H atoms on two water molecules coordinating to the sodium atom (O4w and O5w) did not refine to chemically sensible positions and were not included in the final refinement.

[2] SHELXTL v5.1, Bruker-AXS, Inc., Madison, WI, (1998).

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Crystallographic Tables:

Table 1. Crystal data and structure refinement for **1**.

Identification code	datat	
Empirical formula	NaNi3O21S2C16H19	
Formula weight	810.56	
Temperature	117(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.833(2) Å	α= 74.884(3)°.
	b = 11.107(2) Å	β= 89.323(4)°.
	c = 12.615(3) Å	γ = 69.755(3)°.
Volume	1243.2(5) $Å^3$	
Z	2	
Density (calculated)	2.165 Mg/m^3	
Absorption coefficient	1.268 mm^{-1}	
F(000)	410	
Theta range for data collection	1.68 to 28.30°.	
Index ranges	-12<=h<=12, -14<=k<=14, -16<=l<=16	
Reflections collected	9959	
Independent reflections	5513 [R(int) = 0.0206]	
Completeness to theta = 28.30°	89.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5513 / 9 / 415	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0790	
R indices (all data)	R1 = 0.0371, wR2 = 0.0811	
Largest diff. peak and hole	0.799 and -0.646 $e.Å^{-3}$	

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	8336(1)	3295(1)	7016(1)	8(1)
Ni(2)	6279(1)	3568(1)	5183(1)	8(1)
Ni(3)	7004(1)	1146(1)	7854(1)	9(1)
S(1)	7290(1)	4619(1)	2727(1)	10(1)
S(2)	3995(1)	442(1)	8111(1)	10(1)
Na(1)	4402(1)	2428(1)	9711(1)	21(1)
O(1)	10889(2)	-1230(2)	2443(2)	10(1)
O(2)	9945(2)	-714(2)	3974(2)	14(1)
O(3)	8091(2)	3427(2)	-1410(2)	13(1)
O(4)	6965(2)	1952(2)	-838(2)	12(1)
O(5)	6566(2)	5837(2)	1869(2)	18(1)
O(6)	8547(2)	4658(2)	3334(2)	14(1)
O(7)	6256(2)	4243(2)	3476(2)	13(1)
O(8)	3389(2)	-1737(2)	4963(2)	12(1)
O(9)	2905(2)	-171(2)	3308(2)	12(1)
O(10)	2307(2)	4675(2)	3553(2)	13(1)
O(11)	4013(2)	4443(2)	4846(2)	9(1)
O(12)	4940(2)	1153(2)	8325(2)	12(1)
O(13)	4676(2)	-999(2)	8497(2)	15(1)
O(14)	2591(2)	968(2)	8551(2)	14(1)
O(1W)	10446(2)	3193(2)	7153(2)	16(1)
O(2W)	8510(2)	3131(2)	5397(2)	11(1)
O(3W)	7889(2)	-587(2)	9103(2)	15(1)
O(4W)	1943(3)	3186(2)	10188(2)	37(1)
O(5W)	4273(4)	3812(4)	11253(4)	82(1)
O(6W)	456(3)	4864(3)	11368(3)	42(1)
O(1H)	6390(2)	3038(2)	6829(2)	9(1)
C(1)	9246(3)	969(3)	2280(2)	10(1)
C(2)	8884(3)	1191(3)	1162(2)	11(1)
C(3)	8091(3)	2477(3)	508(2)	10(1)
C(4)	7662(3)	3554(2)	971(2)	11(1)

C(5)	7984(3)	3302(2)	2099(2)	11(1)
C(6)	8755(3)	2027(3)	2763(2)	11(1)
C(7)	10081(3)	-415(3)	2965(2)	11(1)
C(8)	7680(3)	2644(3)	-674(2)	10(1)
C(9)	3177(3)	444(3)	4955(2)	10(1)
C(10)	3032(3)	1750(2)	4374(2)	10(1)
C(11)	3251(3)	2603(2)	4943(2)	9(1)
C(12)	3564(3)	2176(2)	6083(2)	10(1)
C(13)	3653(3)	890(3)	6658(2)	10(1)
C(14)	3477(3)	18(2)	6098(2)	10(1)
C(15)	3134(3)	-568(3)	4348(2)	10(1)
C(16)	3184(3)	4005(2)	4382(2)	10(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

Ni(1)-O(3)#1	2.0340(19)
Ni(1)-O(10)#2	2.0439(18)
Ni(1)-O(1W)	2.045(2)
Ni(1)-O(1H)	2.0552(18)
Ni(1)-O(1)#3	2.0729(18)
Ni(1)-O(2W)	2.097(2)
Ni(1)-Ni(2)	2.9756(7)
Ni(2)-O(1H)	1.9986(19)
Ni(2)-O(8)#4	2.0020(18)
Ni(2)-O(2W)	2.081(2)
Ni(2)-O(7)	2.0846(19)
Ni(2)-O(11)	2.0971(19)
Ni(2)-O(11)#2	2.1177(18)
Ni(3)-O(9)#4	2.0216(19)
Ni(3)-O(1H)	2.0437(18)
Ni(3)-O(3W)	2.058(2)
Ni(3)-O(4)#1	2.0658(19)
Ni(3)-O(12)	2.1053(19)
Ni(3)-O(1)#3	2.1303(18)
S(1)-O(5)	1.4476(19)
S(1)-O(7)	1.4713(19)
S(1)-O(6)	1.480(2)
S(1)-C(5)	1.769(3)
S(2)-O(13)	1.4511(19)
S(2)-O(14)	1.466(2)
S(2)-O(12)	1.4787(18)
S(2)-C(13)	1.773(3)
Na(1)-O(5)#2	2.316(2)
Na(1)-O(13)#5	2.374(2)
Na(1)-O(4W)	2.396(3)
Na(1)-O(12)	2.469(2)
Na(1)-O(4)#1	2.517(2)
Na(1)-O(5W)	2.754(4)
O(1)-C(7)	1.298(3)

O(1)-Ni(1)#3	2.0729(18)
O(1)-Ni(3)#3	2.1303(18)
O(2)-C(7)	1.247(3)
O(3)-C(8)	1.263(3)
O(3)-Ni(1)#6	2.0340(19)
O(4)-C(8)	1.261(3)
O(4)-Ni(3)#6	2.0658(19)
O(4)-Na(1)#6	2.517(2)
O(5)-Na(1)#2	2.316(2)
O(8)-C(15)	1.267(3)
O(8)-Ni(2)#4	2.0020(18)
O(9)-C(15)	1.267(3)
O(9)-Ni(3)#4	2.0216(19)
O(10)-C(16)	1.250(3)
O(10)-Ni(1)#2	2.0439(18)
O(11)-C(16)	1.295(3)
O(11)-Ni(2)#2	2.1177(18)
O(13)-Na(1)#5	2.374(2)
C(1)-C(2)	1.394(4)
C(1)-C(6)	1.399(4)
C(1)-C(7)	1.495(3)
C(2)-C(3)	1.400(4)
C(3)-C(4)	1.400(4)
C(3)-C(8)	1.496(4)
C(4)-C(5)	1.395(4)
C(5)-C(6)	1.391(4)
C(9)-C(14)	1.395(4)
C(9)-C(10)	1.402(3)
C(9)-C(15)	1.528(4)
C(10)-C(11)	1.401(4)
C(11)-C(12)	1.393(4)
C(11)-C(16)	1.512(3)
C(12)-C(13)	1.396(3)
C(13)-C(14)	1.393(4)

O(3)#1-Ni(1)-O(10)#2	90.47(8)

O(3)#1-Ni(1)-O(1W)	90.84(8)
O(10)#2-Ni(1)-O(1W)	89.25(8)
O(3)#1-Ni(1)-O(1H)	94.45(8)
O(10)#2-Ni(1)-O(1H)	100.45(7)
O(1W)-Ni(1)-O(1H)	168.88(8)
O(3)#1-Ni(1)-O(1)#3	91.11(7)
O(10)#2-Ni(1)-O(1)#3	176.49(7)
O(1W)-Ni(1)-O(1)#3	87.60(7)
O(1H)-Ni(1)-O(1)#3	82.54(7)
O(3)#1-Ni(1)-O(2W)	177.47(7)
O(10)#2-Ni(1)-O(2W)	90.46(7)
O(1W)-Ni(1)-O(2W)	91.52(8)
O(1H)-Ni(1)-O(2W)	83.06(7)
O(1)#3-Ni(1)-O(2W)	88.09(7)
O(3)#1-Ni(1)-Ni(2)	133.43(6)
O(10)#2-Ni(1)-Ni(2)	84.39(5)
O(1W)-Ni(1)-Ni(2)	135.14(6)
O(1H)-Ni(1)-Ni(2)	42.04(5)
O(1)#3-Ni(1)-Ni(2)	96.77(5)
O(2W)-Ni(1)-Ni(2)	44.36(5)
O(1H)-Ni(2)-O(8)#4	95.14(7)
O(1H)-Ni(2)-O(2W)	84.88(8)
O(8)#4-Ni(2)-O(2W)	90.93(8)
O(1H)-Ni(2)-O(7)	174.71(7)
O(8)#4-Ni(2)-O(7)	89.17(8)
O(2W)-Ni(2)-O(7)	92.01(7)
O(1H)-Ni(2)-O(11)	99.20(7)
O(8)#4-Ni(2)-O(11)	100.54(7)
O(2W)-Ni(2)-O(11)	167.37(7)
O(7)-Ni(2)-O(11)	82.97(7)
O(1H)-Ni(2)-O(11)#2	90.93(7)
O(8)#4-Ni(2)-O(11)#2	173.66(7)
O(2W)-Ni(2)-O(11)#2	87.76(7)
O(7)-Ni(2)-O(11)#2	84.67(7)
O(11)-Ni(2)-O(11)#2	80.26(7)
O(1H)-Ni(2)-Ni(1)	43.52(5)

O(8)#4-Ni(2)-Ni(1)	107.72(6)
O(2W)-Ni(2)-Ni(1)	44.81(5)
O(7)-Ni(2)-Ni(1)	132.03(5)
O(11)-Ni(2)-Ni(1)	133.82(5)
O(11)#2-Ni(2)-Ni(1)	75.56(5)
O(9)#4-Ni(3)-O(1H)	97.97(7)
O(9)#4-Ni(3)-O(3W)	93.50(8)
O(1H)-Ni(3)-O(3W)	166.23(8)
O(9)#4-Ni(3)-O(4)#1	174.02(7)
O(1H)-Ni(3)-O(4)#1	88.00(7)
O(3W)-Ni(3)-O(4)#1	80.62(8)
O(9)#4-Ni(3)-O(12)	95.84(7)
O(1H)-Ni(3)-O(12)	98.74(7)
O(3W)-Ni(3)-O(12)	87.60(8)
O(4)#1-Ni(3)-O(12)	82.91(7)
O(9)#4-Ni(3)-O(1)#3	91.40(7)
O(1H)-Ni(3)-O(1)#3	81.41(7)
O(3W)-Ni(3)-O(1)#3	90.74(7)
O(4)#1-Ni(3)-O(1)#3	89.76(7)
O(12)-Ni(3)-O(1)#3	172.65(7)
O(5)-S(1)-O(7)	111.48(12)
O(5)-S(1)-O(6)	113.25(11)
O(7)-S(1)-O(6)	111.90(11)
O(5)-S(1)-C(5)	108.15(12)
O(7)-S(1)-C(5)	104.96(11)
O(6)-S(1)-C(5)	106.57(12)
O(13)-S(2)-O(14)	113.59(11)
O(13)-S(2)-O(12)	113.23(11)
O(14)-S(2)-O(12)	108.93(11)
O(13)-S(2)-C(13)	108.16(12)
O(14)-S(2)-C(13)	106.74(12)
O(12)-S(2)-C(13)	105.68(11)
O(5)#2-Na(1)-O(13)#5	168.48(9)
O(5)#2-Na(1)-O(4W)	82.24(9)
O(13)#5-Na(1)-O(4W)	93.89(9)
O(5)#2-Na(1)-O(12)	80.58(7)

O(13)#5-Na(1)-O(12)	110.73(8)
O(4W)-Na(1)-O(12)	117.56(9)
O(5)#2-Na(1)-O(4)#1	93.03(8)
O(13)#5-Na(1)-O(4)#1	89.58(7)
O(4W)-Na(1)-O(4)#1	172.33(9)
O(12)-Na(1)-O(4)#1	67.25(7)
O(5)#2-Na(1)-O(5W)	101.10(10)
O(13)#5-Na(1)-O(5W)	67.38(10)
O(4W)-Na(1)-O(5W)	71.80(11)
O(12)-Na(1)-O(5W)	170.63(11)
O(4)#1-Na(1)-O(5W)	103.40(10)
C(7)-O(1)-Ni(1)#3	126.40(15)
C(7)-O(1)-Ni(3)#3	116.62(15)
Ni(1)#3-O(1)-Ni(3)#3	93.32(7)
C(8)-O(3)-Ni(1)#6	124.05(17)
C(8)-O(4)-Ni(3)#6	127.99(17)
C(8)-O(4)-Na(1)#6	120.21(17)
Ni(3)#6-O(4)-Na(1)#6	104.09(8)
S(1)-O(5)-Na(1)#2	170.05(13)
S(1)-O(7)-Ni(2)	134.27(12)
C(15)-O(8)-Ni(2)#4	138.87(18)
C(15)-O(9)-Ni(3)#4	132.45(16)
C(16)-O(10)-Ni(1)#2	123.20(16)
C(16)-O(11)-Ni(2)	126.55(16)
C(16)-O(11)-Ni(2)#2	128.97(16)
Ni(2)-O(11)-Ni(2)#2	99.74(7)
S(2)-O(12)-Ni(3)	133.68(12)
S(2)-O(12)-Na(1)	121.12(11)
Ni(3)-O(12)-Na(1)	104.52(8)
S(2)-O(13)-Na(1)#5	130.95(12)
Ni(2)-O(2W)-Ni(1)	90.83(7)
Ni(2)-O(1H)-Ni(3)	127.14(9)
Ni(2)-O(1H)-Ni(1)	94.44(7)
Ni(3)-O(1H)-Ni(1)	96.47(8)
C(2)-C(1)-C(6)	119.8(2)
C(2)-C(1)-C(7)	119.5(2)

C(6)-C(1)-C(7)	120.5(2)
C(1)-C(2)-C(3)	120.5(2)
C(4)-C(3)-C(2)	120.1(2)
C(4)-C(3)-C(8)	121.9(2)
C(2)-C(3)-C(8)	118.0(2)
C(5)-C(4)-C(3)	118.5(2)
C(6)-C(5)-C(4)	122.0(2)
C(6)-C(5)-S(1)	118.7(2)
C(4)-C(5)-S(1)	119.20(19)
C(5)-C(6)-C(1)	119.0(2)
O(2)-C(7)-O(1)	124.8(2)
O(2)-C(7)-C(1)	119.0(2)
O(1)-C(7)-C(1)	116.2(2)
O(4)-C(8)-O(3)	125.9(3)
O(4)-C(8)-C(3)	115.6(2)
O(3)-C(8)-C(3)	118.5(2)
C(14)-C(9)-C(10)	120.2(2)
C(14)-C(9)-C(15)	118.7(2)
C(10)-C(9)-C(15)	120.9(2)
C(11)-C(10)-C(9)	119.4(2)
C(12)-C(11)-C(10)	120.4(2)
C(12)-C(11)-C(16)	116.3(2)
C(10)-C(11)-C(16)	123.3(2)
C(11)-C(12)-C(13)	119.5(2)
C(14)-C(13)-C(12)	120.6(2)
C(14)-C(13)-S(2)	122.60(19)
C(12)-C(13)-S(2)	116.8(2)
C(13)-C(14)-C(9)	119.7(2)
O(9)-C(15)-O(8)	127.6(2)
O(9)-C(15)-C(9)	117.7(2)
O(8)-C(15)-C(9)	114.6(2)
O(10)-C(16)-O(11)	124.8(2)
O(10)-C(16)-C(11)	119.2(2)
O(11)-C(16)-C(11)	116.0(2)

Symmetry transformations used to generate equivalent atoms:

Supplementary Material (ESI) for Chemical Communications

#1 x,y,z+1 #2 -x+1,-y+1,-z+1 #3 -x+2,-y,-z+1

#4 -x+1,-y,-z+1 #5 -x+1,-y,-z+2 #6 x,y,z-1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for datat. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	10(1)	7(1)	7(1)	-1(1)	-1(1)	-3(1)
Ni(2)	10(1)	6(1)	7(1)	-1(1)	-1(1)	-2(1)
Ni(3)	11(1)	8(1)	7(1)	-2(1)	0(1)	-3(1)
S(1)	15(1)	7(1)	8(1)	-2(1)	1(1)	-2(1)
S(2)	11(1)	9(1)	8(1)	-1(1)	-1(1)	-4(1)
Na(1)	23(1)	22(1)	13(1)	3(1)	-2(1)	-7(1)
O(1)	8(1)	9(1)	11(1)	-3(1)	1(1)	-2(1)
O(2)	16(1)	11(1)	11(1)	-1(1)	0(1)	0(1)
O(3)	21(1)	12(1)	9(1)	-2(1)	2(1)	-8(1)
O(4)	15(1)	14(1)	10(1)	-5(1)	1(1)	-7(1)
O(5)	27(1)	9(1)	10(1)	-1(1)	-1(1)	0(1)
O(6)	19(1)	14(1)	11(1)	-4(1)	2(1)	-9(1)
O(7)	13(1)	14(1)	10(1)	-3(1)	1(1)	-3(1)
O(8)	17(1)	9(1)	11(1)	-3(1)	1(1)	-5(1)
O(9)	15(1)	10(1)	10(1)	-4(1)	0(1)	-4(1)
O(10)	17(1)	9(1)	10(1)	0(1)	-4(1)	-5(1)
O(11)	11(1)	8(1)	10(1)	-3(1)	1(1)	-3(1)
O(12)	13(1)	13(1)	10(1)	-4(1)	-1(1)	-6(1)
O(13)	20(1)	10(1)	12(1)	-1(1)	0(1)	-3(1)
O(14)	13(1)	17(1)	11(1)	-1(1)	2(1)	-5(1)
O(1W)	13(1)	12(1)	21(1)	2(1)	-3(1)	-6(1)
O(2W)	12(1)	8(1)	11(1)	-1(1)	3(1)	-2(1)
O(3W)	19(1)	11(1)	12(1)	-2(1)	2(1)	-4(1)
O(4W)	52(2)	19(1)	39(2)	-8(1)	25(1)	-11(1)
O(5W)	75(3)	54(2)	105(3)	-10(2)	-22(2)	-15(2)
O(6W)	49(2)	46(2)	55(2)	-32(2)	27(2)	-34(1)
O(1H)	9(1)	8(1)	10(1)	-4(1)	1(1)	-2(1)
C(1)	10(1)	11(1)	9(1)	-3(1)	1(1)	-4(1)
C(2)	10(1)	9(1)	13(1)	-5(1)	2(1)	-3(1)
C(3)	10(1)	12(1)	9(1)	-3(1)	1(1)	-5(1)
C(4)	13(1)	7(1)	10(1)	-1(1)	1(1)	-2(1)

C(5)	13(1)	10(1)	10(1)	-5(1)	3(1)	-5(1)
C(6)	12(1)	13(1)	8(1)	-3(1)	0(1)	-3(1)
C(7)	10(1)	11(1)	12(1)	-2(1)	-2(1)	-5(1)
C(8)	10(1)	9(1)	10(1)	-4(1)	1(1)	0(1)
C(9)	9(1)	12(1)	11(1)	-4(1)	0(1)	-4(1)
C(10)	9(1)	10(1)	9(1)	-3(1)	0(1)	-3(1)
C(11)	10(1)	7(1)	10(1)	-1(1)	1(1)	-2(1)
C(12)	9(1)	9(1)	11(1)	-4(1)	0(1)	-2(1)
C(13)	10(1)	11(1)	8(1)	-2(1)	0(1)	-3(1)
C(14)	10(1)	7(1)	11(1)	-2(1)	1(1)	-2(1)
C(15)	7(1)	11(1)	13(1)	-4(1)	2(1)	-3(1)
C(16)	10(1)	9(1)	10(1)	-2(1)	3(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for datat.

	x	y	z	U(eq)
H(1WA)	11040(30)	2580(30)	7610(20)	19
H(1WB)	10790(30)	3760(30)	6980(30)	19
H(2WA)	8840(30)	3520(30)	4920(20)	13
H(2WB)	9000(30)	2335(19)	5490(30)	13
H(3WA)	7960(40)	-1310(20)	9060(30)	18
H(3WB)	7660(40)	-460(30)	9689(19)	18
H(6WA)	870(40)	5430(40)	11350(40)	50
H(6WB)	430(50)	4470(40)	12041(19)	50
H(1OH)	5740(30)	3570(20)	7000(30)	11
H(2)	9171	480	850	13
H(4)	7173	4418	536	13
H(6)	8943	1879	3516	13
H(10)	2791	2047	3616	12
H(12)	3713	2744	6459	12
H(14)	3559	-844	6484	11

Thermogravimetric analysis (TGA) was conducted on a TA instruments SDT 2960 under nitrogen at the heating rate of 5 °C/min from room temperature to 370 or 800 °C.

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