

Crystal structure of kambaldaite, $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$

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Abstract

A new carbonate mineral, kambaldaite, with the ideal formula $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$, is hexagonal, $P6_3$, $a = 10.340(3)$, $c = 6.097(2)\text{\AA}$; $Z = 1$. The structure has been determined from single crystal X-ray diffractometer data, and refined by full matrix least squares to a residual of 0.048 for 1157 independent "observed" reflections. Distorted NiO_6 "octahedra" are linked in a three-dimensional edifice with bridging carbonate and hydroxyl groups; Ni–O range between 2.022(5)–2.191(5) \AA with O–Ni–O angles as small as 80.5(2)°. Columnar tunnels through the structure with a free pore diameter of $\sim 5\text{\AA}$ about the principal cell axis are occupied by arrays of sodium atoms with octahedral environments of bridging water molecules; Na–O are 2.312(8) and 2.321(8) \AA with O–Na–O angles as small as 81.2(4)°.

Introduction

The description of kambaldaite, a new hydrated sodium/nickel basic carbonate mineral from Kambalda in Western Australia, has been presented in the preceding paper by Nickel and Robinson (1985). The present paper reports the determination of its crystal structure by single crystal X-ray diffraction methods.

Structure determination

Crystal data

$\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O} \equiv \text{C}_6\text{H}_{18}\text{Na}_2\text{Ni}_8\text{O}_{30}$, $M = 1085.7$. Hexagonal, space group $P6_3$ (C_6^6 , No. 173), $a = 10.340(3)$, $c = 6.097(2)\text{\AA}$, $U = 564.6(3)\text{\AA}^3$. D_c ($Z = 1$) = 3.19 g cm^{-3} . $F(000) = 540$. μ_{Mo} = 66.6 cm^{-1} .

Experimental details

A hexagonal prism $\sim 0.1 \text{ mm}$ thick and $\sim 0.1 \text{ mm}$ in length was mounted on a Syntex $P2_1$ four-circle diffractometer after examination by Weissenberg photographic methods. Cell parameters were obtained from 12 axial reflections with $2\theta \sim 40^\circ$. A unique data set was measured at 295 K within the limit $2\theta_{\text{max}} = 100^\circ$ using a conventional $2\theta/\theta$ scan mode, with a monochromatic $\text{MoK}\alpha$ radiation source ($\lambda = 0.71069\text{\AA}$). 2265 independent reflections were measured; of these 1157 with $I > 3\sigma(I)$ were used in the structure determination after the application of analytical absorption correction. The structure was solved by the heavy atom method, and refined by full matrix least squares using anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were located in difference maps and refined in (x, y, z) with U (isotropic) constrained at estimated values. At convergence, residuals R, R' were 0.048, 0.051, reflection weights being $(\sigma^2(F_o) + 0.0005(F_o)^2)^{-1}$; for the alternative chirality R was 0.048. Na^+ excepted, neutral complex scattering factors were used (Ibers and Hamilton, 1974). Computation used

the X-RAY program system (Stewart, 1976) implemented on a Perkin-Elmer 3240 computer. Observed and calculated structure factor amplitudes are given in Table 1;¹ atomic coordinates and thermal parameters are presented in Table 2. A projection of the structure down the c axis is shown in Figure 1, while a projection of the infinite $\text{Na}_2(\text{H}_2\text{O})_6$ column along the non-unique axis is given in Figure 2.

Description of the structure

The structure determination suggests the $\text{Na}_2\text{Ni}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 6\text{H}_2\text{O}$ stoichiometry for kambaldaite. The deviation of the stoichiometry from this ideal composition suggested by the analysis reported in the previous paper (Nickel and Robinson, 1985) was explored during refinement by allowing the population of the most deviant element, sodium, to refine as an unconstrained variable. Since the population did not deviate significantly from one, it was restored and constrained at that value. Note, however, that the "impurity" element present in the greatest proportion is magnesium, and since this is iso-electronic with sodium, its presence replacing Na might be expected to have little effect on the refinement. In this case some disorder may be introduced into the structure which would probably be only reflected as higher than normal thermal parameters in consequence of different metal–oxygen distances. Some "streaking" of the reflections was evident in the profiles observed both in Weissenberg photographs and diffractometer data, and we note that the highest non-hydrogen atom thermal parame-

¹ To receive a copy of Table 1, order Document Am-85-257 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$5.00 in advance for the microfiche.

Table 2. Atom parameters*

Atom	\bar{x}	\bar{y}	\bar{z}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Metal atoms									
Na	0	0	0.3745(11)	21.1(-)	21.1(-)	13.3(21)	10.6(6)	-	-
Ni(1)	0.51259(7)	-0.00191(8)	$\frac{1}{2}$ **	7.2(2)	5.3(2)	6.7(2)	2.0(2)	0.5(4)	0.1(3)
Ni(2)	$\frac{2}{3}$	$\frac{1}{3}$	0.6374(3)	5.9(-)	5.9(-)	7.9(5)	3.0(1)	-	-
Carbonate group									
C	0.7796(5)	0.2172(6)	0.0080(11)	3(1)	7(2)	8(2)	2(1)	0(2)	1(2)
O(3)	0.7324(4)	0.1386(5)	0.1801(8)	5(1)	9(1)	10(2)	0(1)	0(1)	2(1)
O(4)	0.7015(5)	0.1836(4)	-0.1705(7)	8(1)	10(2)	7(2)	4(1)	-2(1)	0(1)
O(5)	0.9129(5)	0.3343(4)	0.0070(8)	5(1)	9(2)	9(1)	2(1)	0(1)	1(2)
Hydroxyl group									
O(2)	0.5188(5)	0.1377(4)	0.4873(7)	10(1)	6(1)	6(2)	6(1)	-1(1)	-1(1)
H(2)	0.467(10)	0.159(10)	0.433(17)	15(-)					
Water molecule									
O(1)	0.0998(7)	0.1948(6)	0.1233(14)	20(2)	16(2)	37(3)	8(2)	0(3)	0(3)
H(1A)	0.081(12)	0.237(12)	0.107(20)	22(-)					
H(1B)	0.170(10)	0.234(12)	0.179(18)	22(-)					

*Thermal parameters are of the form: $\exp(-2\pi^2(U_{11}h^2a^2 + \dots + 2U_{23}k1b*c*))$ and are multiplied by 10^3 (\AA^2)

**Defines origin

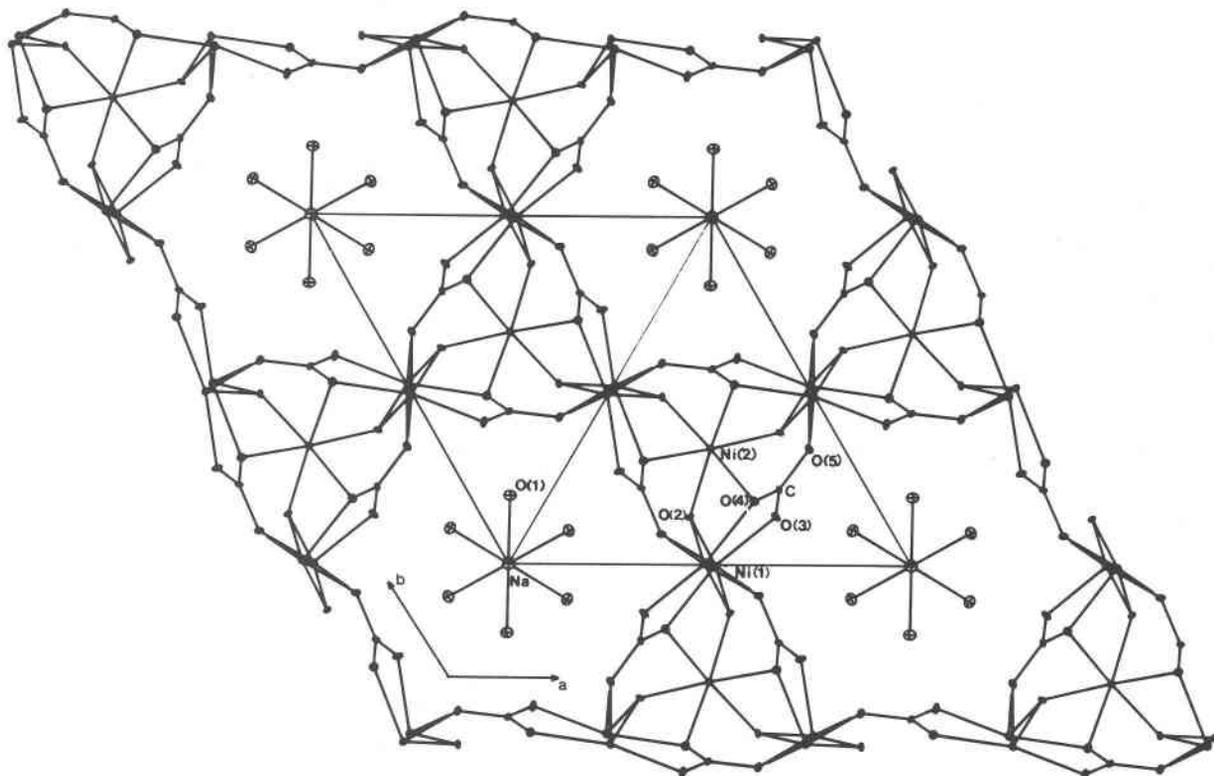


Fig. 1. Projection of the structure of kambaldaite down c . 20% probability thermal ellipsoids are shown for the non-hydrogen atoms.

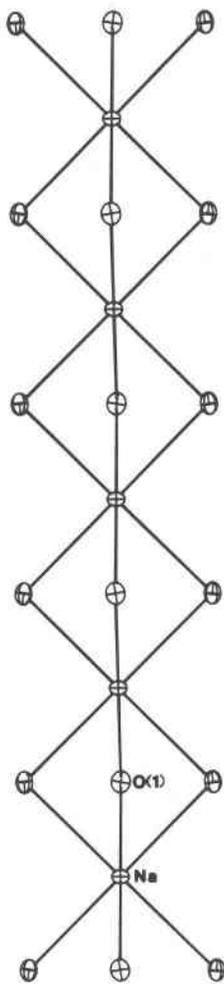


Fig. 2. A projection of the polymeric $\text{Na}_2(\text{H}_2\text{O})_6$ array, normal to the ac plane.

ters in the structure are those for the sodium atom and the water molecule. By contrast, the thermal parameters of other possible sites for magnesium, namely those occupied principally by the nickel atoms, are the lowest in the structure. While this tends to suggest that any magnesium impurities present may be associated with the sodium ion sites, it should be noted that the sodium ions and their immediate neighboring water molecules are not locked rigidly into the three-dimensional edifice as is the rest of the structure, so that higher than normal thermal motion for these atoms might therefore reasonably be expected.

The structure is seen in projection down c in Figure 1, and it is recognized that it may be described in terms of two components. The first is a one-dimensional polymeric cation array of stoichiometry $\text{Na}_2(\text{H}_2\text{O})_6$ occupying tunnels in the lattice along the c axes with a free pore diameter of ca. 5\AA surrounding these. The second is the tunnel structure itself, a three-dimensional polymeric anionic array comprising nickel atoms interlocked by

bridging carbonate and hydroxyl species to form a honeycomb.

Only one sodium atomic position on the Wyckoff a site of point symmetry $\{3\}$ on the 6_3 axis is crystallographically independent, and its environment is generated by the symmetry-related components of only one crystallographically independent water molecule; and it lies in a distorted octahedral coordination environment. The angles between *trans* oxygens approximate to 180° (179.7°), but a number of $\text{O}-\text{Na}-\text{O}$ angles are as low as $81.2(4)^\circ$. Sodium-oxygen distances ($2.312(8)$, $2.321(8)\text{\AA}$) are normal for six-coordinate species. The water molecule hydrogen atoms appear to be hydrogen-bonded to carbonate oxygens ($\text{H}(1)\dots\text{O}(5)$, $(x-1, y, z)$, $2.5(1)$; $\text{H}(2)\dots\text{O}(3)$ ($y-x+1, 1-x, z)$, $2.3(1)\text{\AA}$).

There are two distinct types of nickel atom. $\text{Ni}(2)$ lies on a three-fold axis of Wyckoff b type. The environment of $\text{Ni}(2)$ is generated by three symmetry-related hydroxyl

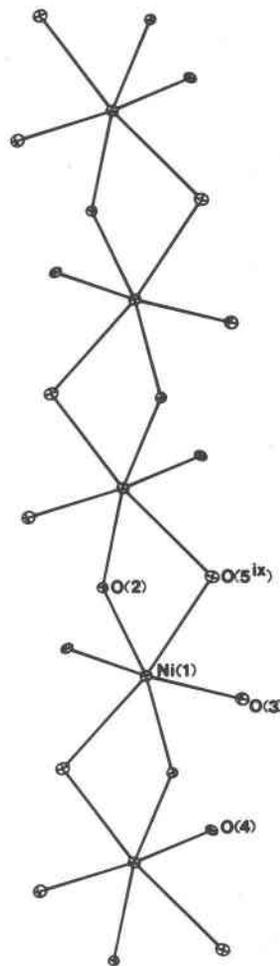


Fig. 3. A projection of the polymer array of $\text{Ni}(1)$ atoms, bridged by hydroxyl and carbonate oxygen atoms, normal to the ac plane.

oxygen atoms at 2.043(4)Å, subtending well-splayed angles of 101.5(2)° at the nickel, and three symmetry related carbonate O(4) oxygen atoms at 2.111(5)Å; these also subtend splayed angles of 92.2(2)° at the nickel. The resultant nickel environment is thus a compressed octahedral array with the nickel displaced slightly from the center toward the face defined by the water molecules. For comparative purposes we note that in nickel sulfate heptahydrate (Healy, Patrick and White, unpublished) nickel-oxygen distances in the pseudo-octahedral array range from 2.035(3) to 2.081(2)Å.

The other nickel atom, Ni(1), lies on a general crystallographic position and is also in distorted octahedral coordination with six oxygen atoms. Two of the coordination sites, *trans* to each other, are occupied by symmetry-related hydroxyl atoms at distances of 2.022(5) and 2.046(5)Å, with O-Ni-O being 171.0(2)°. A second pair of *trans*-sites is occupied by symmetry-related carbonate O(5) oxygen atoms at distances of 2.191(7) and 2.073(7)Å, with O-Ni-O being 172.7(3)°. The last two sites, also *trans*, (O-Ni-O, 167.5(3)°), are occupied by carbonate oxygen atoms O(3,4) at distances of 2.039(4) and 2.122(4)Å. The four carbonate oxygen atoms in the coordination

sphere all arise from different carbonate species. Although the site of Ni(1) is a general position, in fact it lies only slightly displaced from the crystallographic twofold screw axis. Consequently, nickel atoms (Ni(1)) form an array that is almost linear along *c* with a spacing of *c*/2, at *z* = ¼, ¾, etc. Bridging of successive nickel atoms along *c* is accomplished by hydroxyl oxygen atoms O(2) and carbonate oxygen atoms O(5) situated approximately mid-way between them at *z* ~ 0, ½. The carbonate oxygen atoms O(4,3) with *z* coordinates -0.17 and 0.18 respectively, bridge to successive nickel atoms at -¼ and +¼ respectively. The nature of the array is shown in Figure 3.

The hydroxyl ion is of interest, bridging to three independent nickel atoms, two of type Ni(1) and one Ni(2) at distances ranging from 2.022(5)-2.046(5)Å, the shortest of the nickel-oxygen distances in the structure. Consistent with this, the disposition of the Ni₃(OH) unit is pyramidal rather than planar, with the O-Ni-O angle sum well below 360° (334.2°).

The four atoms of the carbonate ion define a good least squares plane ($\sigma = 0.006\text{Å}$). Carbonate O(3) is coordinated to one nickel atom, Ni(1) at 2.039(4)Å, the correspond-

Table 3. Metal atom environments

Distances (Å)		Angles (degrees)		Angles (degrees)	
The sodium environment					
Na-0(1)	2.321(8)	0(1)-Na-0(1 ⁱⁱ)	179.7(2)	0(1 ⁱ)-Na-0(1 ⁱⁱⁱ)	81.6(4)
Na-0(1 ⁱ)	2.312(8)	0(1)-Na-0(1 ⁱⁱ)	81.2(4)	0(1 ⁱⁱ)-Na-0(1 ⁱⁱⁱ)	179.7(2)
		0(1)-Na-0(1 ⁱⁱⁱ)	98.6(3)	0(1 ^{iv})-Na-0(1 ^v)	179.7(3)
The Ni(1) environment					
Ni(1)-0(2)	2.022(5)	0(2)-Ni(1)-0(3)	90.9(2)	0(3)-Ni(1)-0(5 ^{ix})	88.5(2)
Ni(1)-0(3)	2.039(4)	0(2)-Ni(1)-0(4 ^{vi})	96.6(2)	0(4 ^{vi})-Ni(1)-0(2 ^{vii})	80.5(2)
Ni(1)-0(4 ^{vi})	2.122(4)	0(2)-Ni(1)-0(2 ^{vii})	171.0(2)	0(4 ^{vi})-Ni(1)-0(5 ^{viii})	92.8(2)
Ni(1)-0(2 ^{vii})	2.046(5)	0(2)-Ni(1)-0(5 ^{viii})	92.9(2)	0(4 ^{vi})-Ni(1)-0(5 ^{ix})	82.6(2)
Ni(1)-0(5 ^{viii})	2.191(7)	0(2)-Ni(1)-0(5 ^{ix})	82.1(2)	0(2 ^{vii})-Ni(1)-0(5 ^{viii})	78.7(2)
Ni(1)-0(5 ^{ix})	2.073(7)	0(3)-Ni(1)-0(4 ^{vi})	167.5(3)	0(2 ^{vii})-Ni(1)-0(5 ^{ix})	105.8(2)
		0(3)-Ni(1)-0(2 ^{vii})	93.6(2)	0(5 ^{viii})-Ni(1)-0(5 ^{ix})	172.7(3)
		0(3)-Ni(1)-0(5 ^{viii})	96.9(2)		
The Ni(2) environment					
Ni(2)-0(2)	2.043(4)	0(2)-Ni(2)-0(4 ^x)	80.8(2)	0(2)-Ni(2)-0(4 ^{xiii})	85.1(2)
Ni(2)-0(4)	2.111(5)	0(2)-Ni(2)-0(4 ^{xi})	172.4(3)	0(4 ^x)-Ni(2)-0(4 ^{xi})	92.2(3)
		0(2)-Ni(2)-0(2 ^{xii})	101.5(2)		

Transformations of the asymmetric unit:

i	($\bar{x}, \bar{y}, \frac{1}{2}+z$)	iv	($y-x, \bar{x}, z$)	vii	($1-x, \bar{y}, z-\frac{1}{2}$)	x	($x, y, 1+z$)
ii	($\bar{y}, x-y, z$)	v	($x-y, x, \frac{1}{2}+z$)	viii	($y-x+1, 1-x, z$)	xi	($1-y, x-y, 1+z$)
iii	($y, y-x, \frac{1}{2}+z$)	vi	($1-x, \bar{y}, \frac{1}{2}+z$)	ix	($x-y, x-1, \frac{1}{2}+z$)	xii	($1-y, x-y, z$)
						xiii	($1-x+y, 1-x, 1+z$)

Table 4. Oxyanion geometries

Distances	(Å)	Angles (degrees)	Angles (degrees)
The hydroxide			
O(2)-Ni(1)	2.022(5)	Ni(1)-O(2)-Ni(2)	140.2(2)
O(2)-Ni(2)	2.043(4)	Ni(1)-O(2)-Ni(1 ^{VI})	97.6(2)
O(2)-Ni(1 ^{VI})	2.046(5)		
The carbonate			
C-0(3)	1.267(7)	O(3)-C-0(4)	122.4(4)
C-0(4)	1.295(8)	O(3)-C-0(5)	119.3(5)
C-0(5)	1.302(5)	O(4)-C-0(5)	118.3(5)
		Ni(2 ^{XIV})-O(4)-Ni(1 ^{VI})	92.2(1)
		Ni(1 ^{XII})-O(5)-Ni(1 ^{XV})	91.7(1)
		C-0(4)-Ni(2 ^{XIV})	125.5(4)
		C-0(4)-Ni(1 ^{VI})	131.6(3)
		C-0(5)-Ni(1 ^{XII})	125.9(4)
		C-0(5)-Ni(1 ^{XV})	123.9(4)
		C-0(3)-Ni(1)	124.4(4)
Transformations of the asymmetric unit: as for Table 2 plus:			
xiv	(x, y, z-1)	xv	(y+1, y-x+1, z-k)

ing carbon-oxygen distance being the shortest of the three (1.267(7)Å), with the opposing angle O(4)-Ni(1)-O(5) reduced below 120° correspondingly to 118.3(5)°. The other two oxygen atoms bridge pairs of nickel atoms. O(5) bridges successive Ni(1) atoms up the *c* array at 2.191(5) and 2.073(5)Å, O-Ni-O being 91.7(1)°, with the carbon-oxygen distance being the longest of the three (1.302(5)Å), and the opposed O-C-O angle the largest (122.4(4)°). O(4) bridges the two different types of nickel atoms, O(4)-Ni(1,2) being 2.111(5), 2.122(4)Å respectively with the Ni-O-Ni angle being 92.2(2)°. The corresponding carbon-oxygen distance is 1.295(8)Å. Coordination about O(4,5) by the two nickel atoms and the carbon is pyramidal rather than planar with the angle sums at the oxygen atoms being 349.2, 341.5° respectively. Deviations of the coordinated nickel atoms from the above carbonate plane, for Ni(2) (*x*, *y*, *z*-1), Ni(1) (1-*x*, *y*, *z*-½) (attached to O(4)), Ni(1) (1-*y*, *x*-*y*, *z*), (1-*y*, 1-*x*+*y*, *z*-½) (attached to O(5)) and Ni(1) (attached to O(3)) are respectively: 1.265, 0.078; 1.360, 0.201; 0.615Å.

The key overall feature of the structure, namely the infinite honeycomb array, is novel among carbonate species. Somewhat similar arrays have been reported for

other systems based on anionic species conforming to crystallographic or pseudo-three-fold symmetry (e.g., cacoxenite (Moore and Shen, 1983), connellite (McLean and Anthony, 1972)), but in these latter the anion unit is tetrahedral rather than trigonal.

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Manuscript received, October 5, 1983;
 accepted for publication, July 30, 1984.