

Crystal Structure of the β Form of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}^*$

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Abstract

Crystals previously employed for magnetic measurements are shown to be a different form of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Cell parameters of $\beta\text{-Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ are: $a = 7.484$ (2), $b = 10.277$ (3), $c = 5.476$ (1) Å, $\alpha = 101.06$ (3), $\beta = 101.53$ (3), and $\gamma = 68.77$ (3)° with $Z = 2$. The space group is $P\bar{1}$. Parameters were refined by the least-squares method employing 1934 hkl data to $R = 0.049$. The two crystallographically different $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ units are held together by hydrogen bonds. These bonds are believed to be responsible for the small differences observed for the Ni–O bond lengths and the magnetic properties of the two inequivalent Ni^{2+} ions at low temperatures.

Introduction

Recently, Wada, Matsumoto, Amaya & Haseda (1978) reported on the low-temperature magnetic behavior of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. These data are consistent with two kinds of sites for Ni^{2+} ions in a unit cell and, hence, suggested differences from the room-temperature monoclinic structure reported by Gallezot, Weigel & Prettre (hereafter, GWP) (1967). These crystals proved to be a different form of this compound, triclinic in symmetry and with *trans* situated NO_3^- groups about the Ni^{2+} ions compared with *cis* in the monoclinic structure. Small differences in the observed Ni–O(water) bond distances appear to result from the hydrogen bonding in this β form and are consistent with values reported for the monoclinic α form. Our results are presented in this paper.

Experimental details

Crystals of $\beta\text{-Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were grown from aqueous solutions held at about 343 K using a tem-

perature-controlled crystallization bath. Thin rhomboid plates several millimeters on the side were obtained. The X-ray measurements were conducted on fragments cleaved from such a larger specimen. The data crystal did not exceed 0.3 mm in its largest dimension. Lattice constants given in the *Abstract* were obtained by a least-squares fit of 20 different 2θ values obtained on the Picker diffractometer. Intensity data were collected with Mo $K\alpha$ radiation to $2\theta = 57^\circ$ using the θ – 2θ scan technique with a scintillation detector and pulse-height discrimination. Of 1934 intensities measured, 1821 were greater than 3σ where $\sigma = (N_{sc} + K^2 N_b)^{1/2}$ and N_{sc} , N_b and K are the total scan count, background counts and the time ratio of the scan to background, respectively. No correction for absorption was included for our irregular crystal specimen ($\mu = 2.38 \text{ mm}^{-1}$).

Structure determination

Initial positional parameters were determined for two different models from a Patterson Fourier synthesis and succeeding electron density difference syntheses. The model with a molecule centered on the Ni^{2+} ion near $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ was eventually discarded in favor of the model with two different molecules centered on Ni^{2+} ions at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. At first the intensity data were subjected to least-squares refinement using isotropic thermal parameters. The function $\omega(F_o - F_c)^2$ with $\omega = 1/\sigma^2$ was minimized. Structure factors were calculated using scattering factors for Ni^{2+} , O, and N computed from Hartree–Fock wave functions (Cromer & Mann, 1968) and, for H, from Stewart, Davidson & Simpson (1965). After the positions of all non-hydrogen atoms had been refined, a difference synthesis showed positions of the H atoms along potential hydrogen bonds. These positional parameters for the H atoms were included with a fixed isotropic thermal parameter in subsequent refinement cycles in which anisotropic thermal parameters for the remaining

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Table 1. Atomic coordinates for β -Ni(NO₃)₂·4H₂O [$\times 10^4$ for heavy atoms, $\times 10^2$ (x and z) and $\times 10^3$ (y) for H]

	x	y	z
Ni(1)	0	0	0
Ni(2)	5000	5000	5000
N(1)	2953 (5)	893 (4)	-1501 (7)
N(2)	2197 (5)	3991 (4)	6613 (7)
O(1)	-2273 (5)	880 (4)	-2726 (6)
O(2)	-629 (6)	2010 (4)	1859 (8)
O(3)	1699 (5)	250 (4)	-2288 (6)
O(4)	3769 (5)	1067 (4)	-3086 (7)
O(5)	3275 (5)	1282 (4)	766 (6)
O(6)	7596 (5)	3722 (4)	6658 (8)
O(7)	5145 (5)	3383 (4)	2073 (6)
O(8)	3775 (5)	4298 (4)	7299 (6)
O(9)	1323 (5)	3966 (4)	8262 (7)
O(10)	1658 (5)	3740 (4)	4341 (6)
H(1)	-18 (1)	50 (9)	-40 (2)
H(2)	-33 (1)	88 (9)	-26 (2)
H(3)	1 (1)	247 (9)	27 (2)
H(4)	8 (1)	211 (9)	12 (2)
H(5)	50 (1)	368 (9)	10 (2)
H(6)	45 (1)	286 (9)	22 (2)
H(7)	86 (1)	394 (9)	72 (2)
H(8)	76 (1)	306 (9)	66 (2)

atoms were used. The final residual value, $R = \sum |F_o| - |F_c| / \sum |F_o|$, was 0.049. The final atomic parameters are listed in Table 1. Computations were performed with the XRAY 76 system (Stewart, 1976).*

Structural results

The crystal structure (Fig. 1) consists of two crystallographically independent Ni(NO₃)₂(H₂O)₄ units which differ in an interesting, but small, way. Each Ni²⁺ ion is surrounded by a slightly distorted octahedron composed of four water molecules and two O atoms belonging to the nitrate ions. The Ni—O bond lengths (Table 2) range from 2.05 to 2.08 Å and will be discussed below. The nitrate ions are *trans* to each other in this β form, whereas in the α form they are *cis* (GWP, 1967). The distortion from octahedral symmetry in each case principally consists of a small compression along one of the [111] directions, *i.e.* through the plane formed by O(1'), O(2) and O(3) for Ni(1) and by O(6), O(7') and O(8') for Ni(2), where the prime refers to atoms related by the inversion center. In both octahedra the [111] axes are approximately along the long diagonal of Fig. 1. The difference

in relative positions of the two octahedra with respect to the unit cell involves the sense of rotation about these [111] axes, in one case clockwise and the other counterclockwise. This then results in slightly different near-neighbors for the water molecules and hence different arrangements of the hydrogen bonds. Note for example in Fig. 1 that the water molecule O(1) is involved in a hydrogen bond from the body-centered unit, from O(6), whereas none of the hydrogens on the origin unit are involved in hydrogen bonds to water molecules of the body-centered unit.

The N—O distances in the nitrate ion differ over the range 1.225 to 1.297 Å. Such large variations are not unusual though and can be correlated with various aspects of the bonding network of the crystal structure. The present values are in good agreement with trends noted for metal—oxygen and hydrogen-bonding interactions (Morosin, 1970). Such trends suggest that the shorter the metal—oxygen bond length, the longer the N—O distance; similarly the shorter the O—H...O distance, the longer the N—O distance.

Hydrogen-bonding interactions vary from 2.807 to 2.969 Å. The positional parameters of the H atoms were refined and yielded O—H distances ranging from 0.66 to 1.11 Å. For O(6), an additional separation of 3.023 (6) Å exists, to O(10), which is a bit shorter than normally observed as a near-neighbor contact distance.

The Ni—O bond lengths are believed to be influenced by the nature of the hydrogen bonding in this structure.

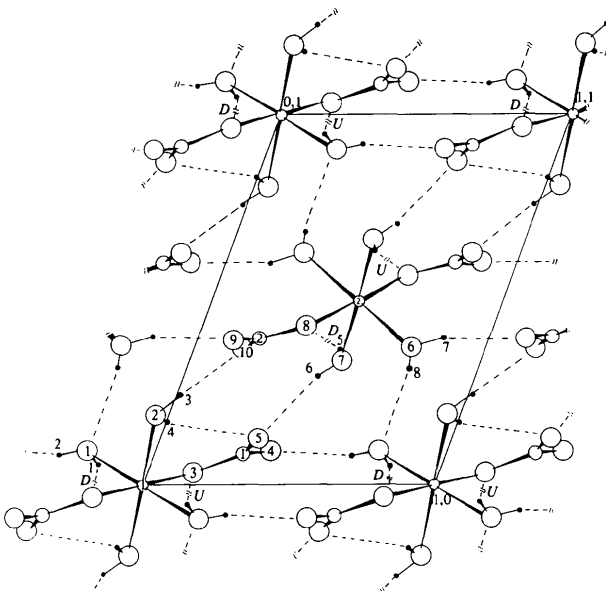


Fig. 1. Crystal structure of β -Ni(NO₃)₂·4H₂O. View along [001]. Small circles represent Ni²⁺, medium-sized circles N of the NO₃⁻ ions, large circles O atoms and solid small circles H atoms. The dashed lines indicate hydrogen-bonding interactions; when such lines are broken, a translation to a unit below (D) or above (U) is required to proceed from the H atom to the O atom.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34695 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic separations and angles*

(a) Nickel environments			
Ni(1)—O(1)	2.080 (3) Å	O(1)—Ni(1)—O(2)	85.4 (1)°
Ni(1)—O(2)	2.050 (4)	O(1)—Ni(1)—O(3)	84.1 (1)
Ni(1)—O(3)	2.062 (4)	O(2)—Ni(1)—O(3)	95.0 (2)
Ni(2)—O(6)	2.056 (3)	O(6)—Ni(2)—O(7)	87.2 (1)
Ni(2)—O(7)	2.064 (3)	O(6)—Ni(2)—O(8)	85.1 (2)
Ni(2)—O(8)	2.058 (4)	O(7)—Ni(2)—O(8)	97.3 (2)
(b) Nitrate ions			
N(1)—O(3)	1.297 (6)	O(3)—N(1)—O(4)	117.2 (4)
N(1)—O(4)	1.227 (7)	O(3)—N(1)—O(5)	119.0 (5)
N(1)—O(5)	1.232 (5)	O(4)—N(1)—O(5)	123.8 (5)
N(2)—O(8)	1.297 (6)	O(8)—N(2)—O(9)	117.9 (4)
N(2)—O(9)	1.225 (6)	O(8)—N(2)—O(10)	118.4 (4)
N(2)—O(10)	1.236 (5)	O(9)—N(2)—O(10)	123.6 (5)
(c) Hydrogen bonding			
O(1)—O(4a)	2.868 (6)	O(4a)—O(1)—O(3b)	98.8 (1)
O(1)—O(3b)	2.807 (5)	H(1)—O(1)—H(2)	122 (9)
O(1)—H(1)	0.80 (9)		
O(1)—H(2)	0.80 (9)		
O(2)—O(5)	2.898 (6)	O(5)—O(2)—O(10)	60.7 (1)
O(2)—O(10)	2.879 (6)	H(3)—O(2)—H(4)	107 (11)
O(2)—H(3)	0.87 (9)		
O(2)—H(4)	1.11 (9)		
O(6)—O(9e)	2.839 (6)	O(9e)—O(6)—O(1c)	109.6 (2)
O(6)—O(1c)	2.969 (6)	H(7)—O(6)—H(8)	120 (10)
O(6)—H(7)	0.82 (9)		
O(6)—H(8)	0.66 (9)		
O(7)—O(5)	2.886 (6)	O(5)—O(7)—O(8d)	91.6 (1)
O(7)—O(8d)	2.818 (5)	H(5)—O(7)—H(6)	122 (9)
O(7)—H(5)	0.70 (9)		
O(7)—H(6)	0.88 (9)		

Symmetry code: (a) $-1 + x, y, z$; (b) $-x, -y, -1 - z$; (c) $1 + x, y, 1 + z$; (d) $x, y, z - 1$; (e) $1 + x, y, z$.

The Ni(1)—O(1) bond length (2.080 Å) is significantly longer than the other three Ni—O(water) [ave. 2.057 (3) Å], probably because O(1) is involved in an additional hydrogen-bonding interaction [with O(6); see Fig. 1]. The α form shows similar results. In that study the 2.086 Å Ni—H₂O(I) and the 2.085 Å Ni—H₂O(III) bond distances are slightly longer than the remaining two Ni—H₂O distances (2.039 and 2.053 Å); both H₂O(I) and H₂O(III) are involved in an

additional hydrogen-bonding interaction.* The values of the Ni—O(NO₃) lengths for the two studies are also in excellent agreement.

The low-temperature magnetic measurements are of particular interest since two different spin-ordered states are observed when a field is applied along either of the two ion axes, † Z_A and Z_B . In the case for Z_A , our specific-heat measurements show a rather sharp and symmetric peak at the transition temperature, suggestive of the behavior of a two-dimensional phase transition. On the other hand, the shape for the Z_B peak is much more rounded. The temperature—magnetic-field phase-boundary characteristics for Z_B are also quite different from Z_A or from the usual behavior for Ni²⁺ reported to date (Wada, Matsumoto, Amaya & Haseda, 1978). The two Z axes make an angle of about 55° even though the two trigonally compressed octahedra are much more closely aligned. The influence of the longer Ni(1)—O(1) bond on the crystal field must, hence, be significant and influence the ion axis of Ni(1). Rationalization of the detailed magnetic behavior on the basis of the structure is not possible at this time.

* In the α form, using the e.s.d. of 0.009 Å reported by GWP for the Ni—O lengths and taking account of the correlation of bonds with common atoms, the difference in the average of the longer bonds, 2.085 Å, from the shorter set, 2.046 Å, is a borderline case in a test for possible significance (Stout & Jensen, 1968).

† The two axes are in the (110) plane with the $[\bar{1}30]$ axis bisecting the 55° angle between Z_A and Z_B and with Z_A normal to $[0\bar{1}1]$.

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