

sin θ/λ values along with absorption and extinction corrections, the thermal parameters should have some validity.

Support of this research by the National Science Foundation (GP-38022X) and Vanderbilt University is gratefully acknowledged.

References

- BERTRAND, J. A. & CARPENTER, D. A. (1966). *Inorg. Chem.* **5**, 514–516.
 BERTRAND, J. A., CARPENTER, D. A. & KALYANARAMAN, A. R. (1971). *Inorg. Chim. Acta*, **5**, 113–114.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 CULLEN, D. L. & LINGAFELTER, E. C. (1971). *Inorg. Chem.* **10**, 1264–1268.
 HARROWFIELD, B. V. & PILBROW, J. R. (1973). *J. Phys. C: Solid State Phys.* **6**, 755–766.

- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
 MILLER, P. T., LENHERT, P. G. & JOESTEN, M. D. (1972). *Inorg. Chem.* **11**, 2221–2227.
 REINEN, D., FRIEBEL, C. & REETZ, K. P. (1972). *J. Solid State Chem.* **4**, 103–114.
 STEWART, J. M. (1967). *X-RAY 67 Program System for X-ray Crystallography for the Univac 1108*, CDC 3600/6600, IBM 360/50, 65, 75, IBM 7094. Technical Report TR-67-58, Computer Science Center, Univ. of Maryland, College Park, Maryland.
 TAKAGI, S., JOESTEN, M. D. & LENHERT, P. G. (1975a). *Acta Cryst.* **B31**, 1970–1972.
 TAKAGI, S., JOESTEN, M. D. & LENHERT, P. G. (1975b). *J. Amer. Chem. Soc.* **97**, 444–445.
 TAKAGI, S., JOESTEN, M. D. & LENHERT, P. G. (1975c). *Acta Cryst.* **B31**, 596–598.
 TAKAGI, S., LENHERT, P. G. & JOESTEN, M. D. (1974). *J. Amer. Chem. Soc.* **96**, 6606–6609.
 WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Oak Ridge National Laboratory Report ORNL-TM-229.
 ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Acta Cryst. (1975). **B31**, 1970

Potassium Barium Hexanitronickelate(II)

BY SHOZO TAKAGI AND MELVIN D. JOESTEN

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, U.S.A.

AND P. GALEN LENHERT

Department of of Physics, Vanderbilt University, Nashville, Tennessee 37235, U.S.A.

(Received 13 January 1975; accepted 24 February 1975)

Abstract. $\text{K}_2\text{BaNi}(\text{NO}_2)_6$, cubic, $Fm\bar{3}$, $a = 10.7800(4)$ Å, at 295 K ($\lambda = 1.54051$ Å), $Z = 4$, $D_x = 2.918$ g cm $^{-3}$. Some crystals appear to have the space group $Fm\bar{3}m$. An independent structure analysis has been carried out for one crystal of each type. The hexanitronickelate ion has $m\bar{3}$ symmetry with a Ni–N bond length of 2.080(2) Å. The N–O bond distance is 1.248(2) Å and the O–N–O angle is 117.2(2)°.

Introduction. Buff-colored crystals of $\text{K}_2\text{BaNi}(\text{NO}_2)_6$ were obtained by the method of Goodgame & Hitchman (1964). Systematic absences (hkl with $h+k$, $k+l$, or $h+l$ odd) and the diffraction symmetry indicate the space group $Fm\bar{3}$. However, some crystals from the same batch show $m\bar{3}m$ Laue symmetry. This paper reports two independent structure studies of the title compound. One data set is from crystal M3 which had $m\bar{3}$ Laue symmetry, the other, from crystal M3M which had $m\bar{3}m$ Laue symmetry.

The true symmetry of the hexanitronickelate(II) ion is $m\bar{3}$. The higher apparent symmetry ($m\bar{3}m$) arises either because of disorder or perhaps from a type of twinning which gives a similar diffraction pattern. These possibilities are considered below.

The cell constants for crystal M3 given above were determined from the least-squares refinement of 2θ , ω and χ values for 18 Cu $K\alpha_1$ reflections ($84^\circ < 2\theta < 85^\circ$) with $\lambda = 1.54051$ Å. The cell constants of crystal M3M, determined with Mo $K\alpha_1$ radiation, were identical. Data collection conditions for both crystals were identical with those used for $\text{K}_2\text{PbNi}(\text{NO}_2)_6$ (Takagi, Joesten & Lenhart, 1975b). Further details of the data crystals, data sets* and refinement parameters are given in Table 1.

The data for crystal M3M were collected first and refinement began with space group $Fm\bar{3}$ and parameters obtained from $\text{K}_2\text{PbNi}(\text{NO}_2)_6$ (Takagi, Joesten & Lenhart, 1975b). We soon discovered that the two crystals were not isostructural as expected and a re-examination of the $\text{K}_2\text{BaNi}(\text{NO}_2)_6$ precession films showed $m\bar{3}m$ symmetry rather than the $m\bar{3}$ symmetry previously seen in other cubic nitrite crystals of the

* A list of structure factors of both crystals (M3, M3M) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30965 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Crystal data*

	Crystal M3M	Crystal M3
Crystal size	0.26 × 0.30 × 0.30 mm	0.15 × 0.21 × 0.22 mm
Crystal volume	0.0149 mm ³	0.0041 mm ³
Number of reflections		
Total measured	2875	2913
Averaged (all $F_o > 0$)	314	489
X-ray exposure time	99 h	180 h
Intensity decrease	6%	8%
X-ray intensity fluct.	0.922%	1.56%
Absorption corrections		
Linear abs. coef.	50.9 cm ⁻¹	50.9 cm ⁻¹
Gaussian integration grid	6 × 6 × 6	6 × 6 × 6
Max. transmission factor	0.426	0.566
Min. transmission factor	0.294	0.423
Final refinement cycle		
Ave. shift/error	0.018	0.013
Max. shift/error	0.064	0.062
R (all refin)	0.015	0.016
$R_w = \frac{\sum w(F_o - F_c)^2}{\sum F_o ^2}$	0.023	0.023
S.E. of an obs.	7.20	3.80
Final difference map		
Max. $\Delta\rho$ (at Ba ²⁺)	1.1 e Å ⁻³	1.0 e Å ⁻³
Min. $\Delta\rho$ (at K ⁺)	-0.9	-0.8
Extinct. parameter (r^*)	0.0795 × 10 ⁻⁴ cm	0.0809 × 10 ⁻⁴ cm

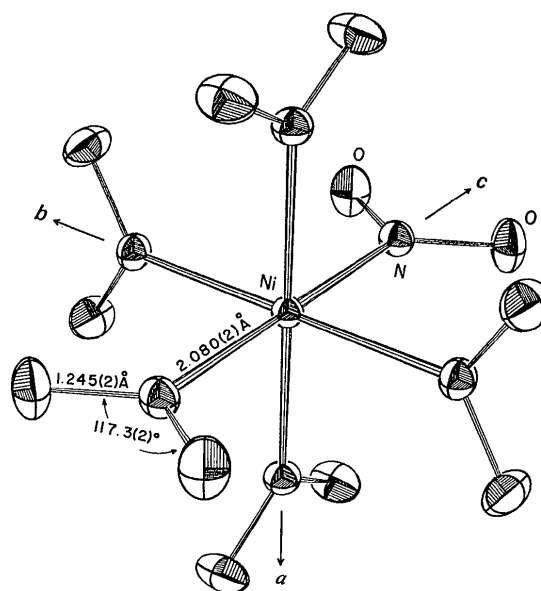


Fig. 1. Hexanitronickelate(II) anion with alternate NO₂ group orientations. Cell axes, bond distances, angles and atomic labeling are shown. Thermal ellipsoids drawn at 50% probability by ORTEP (Johnson, 1965).

type $M_2M'M''(NO_2)_6$. The refinement model was modified to provide $m3m$ symmetry by allowing each NO₂ group to be disordered with 50% occupancy in each position. This model, including the oxygen occupancy factors, was refined to $R=0.017$. Since the alternate NO₂ orientations gave equal occupancy factors, the space group was changed to $Fm3m$ and the refinement repeated with re-averaged data. The residual dropped to 0.015 thus confirming the higher-symmetry space group for crystal M3M. Final parameters are reported in Table 2(a).

More than a dozen crystals were then surveyed in an effort to determine if all $K_2BaNi(NO_2)_6$ crystals show apparent $m3m$ symmetry. About half of those surveyed had $m3$ symmetry. Data for one of these, crystal M3, was collected (see Table 1) and the structure refined in space group $Fm3$. The NO₂ groups were

again found to be disordered but with unequal occupancy in the two alternate positions. Oxygen occupancy was refined initially, then fixed to correspond to the chemical formula. The final parameters are reported in Table 2(b).

Refinement, weights, scattering factors (anomalous dispersion for the heavy atoms) and computer programs are given in Takagi, Joesten & Lenhert (1975b) with final values shown in Table 1.

Discussion. The $K_2BaNi(NO_2)_6$ structure reported here (Fig. 1) was selected for study to allow comparison with $K_2BaCu(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975a) and $K_2PbNi(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975b).

The interatomic distances and angles for both the $K_2BaNi(NO_2)_6$ crystals reported in this paper are given in Table 3. Comparison of these results with

Table 2. *Positional and thermal parameters for $K_2BaNi(NO_2)_6$*

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

(a) Crystal M3M parameters

	Occupancy	x/a	y/b	z/c	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni		0	0	0	0.910 (9)					
Ba		0	0	$\frac{1}{2}$	0.930 (7)					
K		$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.364 (29)					
O	0.5	0	0.09877 (23)	0.25320 (20)	4.61 (14)	1.68 (7)	1.32 (6)	0	0	-0.27 (6)
N		0	0	0.19288 (20)	1.55 (8)	1.55 (8)	1.10 (5)	0	0	0

(b) Crystal M3 parameters

Ni		0	0	0	0.895 (7)					
Ba		0	0	$\frac{1}{2}$	0.917 (5)					
K		$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.375 (24)					
O(1)	0.7334	0	0.09848 (17)	0.25326 (14)	4.09 (9)	1.40 (5)	1.02 (4)	0	0	-0.26 (4)
O(2)	0.2666	0.25309 (56)	0.09995 (74)	0	2.17 (22)	2.84 (27)	7.03 (57)	-0.42 (19)	0	0
N		0	0	0.19290 (16)	1.57 (5)	1.52 (5)	1.04 (4)	0	0	0

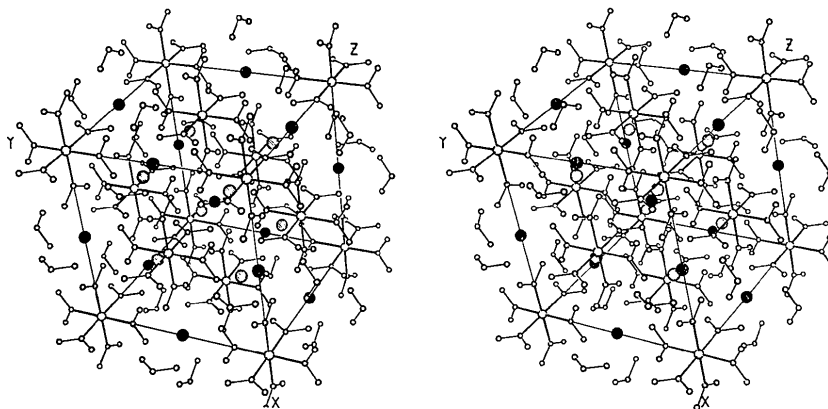


Fig. 2. Stereo view of the unit cell and adjacent groups. Solid circles: Ba^{2+} ; stippled circles: K^+ . Alternate NO_2 group orientations not shown.

corresponding tables in Takagi *et al.* (1975a) and Takagi *et al.* (1975b) shows identical Ni–N and N–O distances in the two $\text{Ni}(\text{NO}_2)_6^{4-}$ ions. The Ba–O distances are nearly identical but the K–O distances vary from 3.082 Å in $\text{K}_2\text{PbNi}(\text{NO}_2)_6$ to 3.240 Å in $\text{K}_2\text{BaCu}(\text{NO}_2)_6$.

Table 3. *Interatomic distances and angles for $\text{K}_2\text{BaNi}(\text{NO}_2)_6$ (crystals M3M and M3)*

	M3M		M3
Ni–N	2.080 (2) Å	N—O(1)	2.079 (2) Å
N–O	1.248 (3)	N—O(2)	1.245 (2)
		Ba—O(1)	1.258 (8)
Ba–O	2.866 (2)	Ba—O(2)	2.864 (2)
		Ba—O(1)	2.871 (6)
K–O	3.151 (1)	K—O(1)	3.151 (1)
		K—O(2)	3.143 (4)
O–N–O	117.2 (2)°	O(1)–N—O(1)	117.0 (2)°
		O(2)–N—O(2)	117.9 (5)

The variation in K–O distances can be rationalized by considering the crystal structure. The $\text{M}'\text{--NO}_2$ bonds are oriented along the crystallographic axes (Fig. 1) and the metal (Ba^{2+} or Pb^{2+}) is located between the NO_2 groups of adjacent $\text{M}''(\text{NO}_2)_6^{4-}$ ions. The unit cell size is thus seen to be determined by the size of the $\text{M}''(\text{NO}_2)_6^{4-}$ group and the M' counter ion. The other counter ion, M, at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, occupies the space between layers of M' and M'' ions with four $\text{M}''(\text{NO}_2)_6^{4-}$ groups arranged tetrahedrally around it (Fig. 2). The K–O distances seem to be a result of the 'pocket' size rather than a factor in determining it.

The apparent $m3m$ symmetry of one of the crystals studied could be due to a random distribution of NO_2 groups rotated 90° away from those shown in Fig. 2. A similar 90° rotation either of randomly distributed $\text{Ni}(\text{NO}_2)_6^{4-}$ ions or of all $\text{Ni}(\text{NO}_2)_6^{4-}$ ions in an extended region of the crystal could explain the higher symmetry. As noted above, all $\text{K}_2\text{BaNi}(\text{NO}_2)_6$ crystals examined show evidence of this 'disorder'. $\text{K}_2\text{PbNi}(\text{NO}_2)_6$ (Takagi *et al.*, 1975b) shows no 'disorder' at all.

We are unable to offer a conclusive argument to explain the presence of 'disorder' in $\text{K}_2\text{BaNi}(\text{NO}_2)_6$

and its absence in $\text{K}_2\text{PbNi}(\text{NO}_2)_6$. However, we note that if an NO_2 group is rotated 90° , the O–O distance between nearest $\text{Ni}(\text{NO}_2)_6$ neighbors is reduced from 3.28 to 2.25 Å if M' is Ba and from 3.15 to 2.12 Å if M' is Pb. This suggests that the short O–O interaction required to alter the $m3$ symmetry is too costly in energy in the Pb crystals but acceptable in the case of the larger Ba counter ion. The corresponding intrion, O–O, distances change from 3.37 to 2.36 Å when one NO_2 group in the $\text{Ni}(\text{NO}_2)_6^{4-}$ ion is rotated 90° . These intra-ion distances are of course the same for crystals with either Ba or Pb counter ions.

An alternative explanation of why $\text{K}_2\text{BaNi}(\text{NO}_2)_6$ shows disorder and $\text{K}_2\text{PbNi}(\text{NO}_2)_6$ does not may be related to the bonding properties of Ba^{2+} and Pb^{2+} rather than to their size. Greater covalent character in the Pb–O bonds may present a significant barrier to NO_2 group rotation independent of the close approach of neighboring O–O atoms.

We conclude that either the short O–O inter-ion distance or the greater covalent character of the Pb–O bond, or both, are important factors in allowing or preventing the introduction of the 'disordered' state. Since the number of short O–O interactions or non-symmetrical PbO_{12} groups would be much greater if the 'disorder' were random, it seems likely that the crystal contains domains or regions of each $\text{Ni}(\text{NO}_2)_6^{4-}$ ion orientation. Such a structure should perhaps be described as a type of twinning.

Support of this research by the National Science Foundation (GP-38022X) and Vanderbilt University is gratefully acknowledged.

References

- GOODGAME, D. M. L. & HITCHMAN, M. A. (1964). *Inorg. Chem.* **3**, 1389–1394.
 JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
 TAKAGI, S., JOESTEN, M. D. & LENHART, P. G. (1975a). *Acta Cryst.* **B31**, 596–598.
 TAKAGI, S., JOESTEN, M. D. & LENHART, P. G. (1975b). *Acta Cryst.* **B31**, 1968–1970.