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Potassium Lead Hexanitronickelate(II)

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Abstract. $K_2PbNi(NO_2)_6$, cubic, *Fm*3, $a=10\cdot5775(8)$ Å, ($\lambda=0\cdot70926$ Å, 295 K), $Z=4$, $D_x=3\cdot480$ g cm^{-3}. It is isomorphous with $K_2PbCu(NO_2)_6$ and $K_2BaCo(NO_2)_6$ at 295 K. The hexanitronickelate(II) ion has *m*3 symmetry with a Ni–N bond length of 2·080(2) Å. The N–O bond distance is 1·245(2) Å and the O–N–O angle is 117·3(2)°.

Introduction. Buff-colored crystals of $K_2PbNi(NO_2)_6$ were obtained by the method of Reinen, Friebel & Reetz (1972). Laue symmetry, systematic absences (*hkl* with $h+k$, $k+l$, or $h+l$ odd) and the expected structure indicate the space group *Fm*3.

The crystal used for data collection measured about $0\cdot15\times0\cdot18\times0\cdot30$ mm and had a volume of 0·0051 mm^3. The cell constants were determined from least-squares refinement of 2θ, ω, and χ values for 18 reflections measured at 2θ angles of about 65° with Mo $K\alpha_1$ radiation. A four-circle automated diffractometer was used to collect intensity data for 2713 reflections (*hkl* and $h\bar{k}\bar{l}$ octants) out to $2\theta=90°$ (Nb-filtered Mo $K\alpha$ radiation with θ–2θ scans at 1° min^{-1}). Symmetry-related observations were averaged to give 462 independent reflections, which were all observed ($F_o>0$). Three monitor reflections showed an intensity decrease of about 1% after 168h of X-ray exposure. Absorption corrections were calculated with the program *ORABS* (Wehe, Busing & Levy, 1962), using a linear absorption coefficient for Mo $K\alpha$ of 163·7 cm^{-1} and a Gaussian grid $10\times10\times10$; maximum and minimum transmission factors were 0·228 and 0·089. Further details of the data collection and reduction methods have been described previously (Miller, Lenhert & Joesten, 1972).

The crystal structure of $K_2PbNi(NO_2)_6$ was refined by using, as starting coordinates, those obtained for the isostructural $K_2PbCu(NO_2)_6$. The Ni, Pb and K atoms were refined isotropically as required by space-group symmetry and the O and N atoms were refined anisotropically along with an isotropic extinction parameter which refined to a value of $0\cdot2233\times10^{-4}$ cm for r^* (Zachariasen, 1968). Atomic scattering factors (for neutral atoms) were those tabulated by Cromer & Mann (1968). Anomalous scattering factors (used for Pb, Ni and K) were those of Cromer & Liberman (1970). The final positional and thermal parameters are given in Table 1.

Full-matrix least-squares refinement on *F* with all 462 reflections gave a conventional *R* of 0·016.† The least-squares weights were based on counting statistics and included the usual instability term with a value of 0·722% (Miller *et al.*, 1972). The final average and maximum shift-to-error ratios for the atomic parameters are 0·004 and 0·015, respectively. The resulting standard error of an observation of unit weight was 4·34. A final difference map showed maximum density of 1·8 eA^{-3} (near K) and minimum values of about −1·8 eA^{-3} (near Ni). Evidence of disorder in the NO_2 groups as observed in $K_2BaNi(NO_2)_6$ by Takagi, Joesten & Lenhert (1975*a*) is absent. Photographic data on about a dozen other $K_2PbNi(NO_2)_6$ crystals confirm that disorder, if present, is rare. Computations except as noted above were carried out with the *X-ray* 67 program (Stewart, 1967) as implemented and updated on the Vanderbilt Sigma 7 computer.

Discussion. The $K_2PbNi(NO_2)_6$ structure reported here (Fig. 1) is one of a series of Cu(II) and Ni(II) nitrite compounds under study in this laboratory. All members of the series, $M_2M'M''(NO_2)_6$, show the same arrangement of the counter ions M and M′, but the symmetry of the $M''(NO_2)_6^{4-}$ cluster differs as

Table 1. *Positional and thermal parameters for* $K_2PbNi(NO_2)_6$

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

	x/a	y/b	z/c	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	0·865 (10)					
Pb	0	0	$\frac{1}{2}$	0·966 (6)					
K	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2·840 (25)					
O	0	0·10056 (16)	0·25785 (16)	3·28 (8)	1·54 (5)	1·33 (5)	0	0	−0·31 (4)
N	0	0	0·19661 (23)	1·33 (7)	1·39 (7)	1·04 (7)	0	0	0

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30964 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

noted below. The objective of the study is to understand those factors which contribute to the three observed configurations of the $Cu(NO_2)_6^{4-}$ cluster.

The cubic $K_2PbCu(NO_2)_6$ crystals have six equal Cu–N distances at 295 K (Cullen & Lingafelter, 1971) but at 281 K a transition to an orthorhombic lattice is observed (Harrowfield & Pilbrow, 1973) where the environment of the Cu(II) is compressed tetragonal (Takagi, Lenhert & Joesten, 1974). $Rb_2PbCu(NO_2)_6$ crystals are orthorhombic at 295 K and also have a compressed tetragonal Cu(II) environment (Takagi, Joesten & Lenhert, 1975*b*). However, with other counter ions, *e.g.*, $K_2CaCu(NO_2)_6$ (Takagi *et al.*, 1974) and $K_2BaCu(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975*c*), the crystals are orthorhombic with Cu(II) in an elongated tetragonal environment showing four equal short Cu–N distances and two long ones.

The $K_2PbNi(NO_2)_6$ crystals were studied because six-coordinate Ni(II) is not a Jahn–Teller ion and it seemed worthwhile to demonstrate that the tetragonal configuration observed for the CuN_6 group was not due to the influence of the counter ions. The Ni(II) crystals are found to retain their cubic symmetry (as shown by single-crystal X-ray photographs) down to 130 K. This is in contrast to the behavior of the $K_2PbCu(NO_2)_6$ crystals mentioned above and the $K_2BaCo(NO_2)_6$ crystals studied by Bertrand, Carpenter & Kalyanaraman (1971) which are also cubic at 295 K but orthorhombic at 233 K. These observations demonstrate the crucial role of the Jahn–Teller ions Cu(II) and Co(II) in the phase transition.

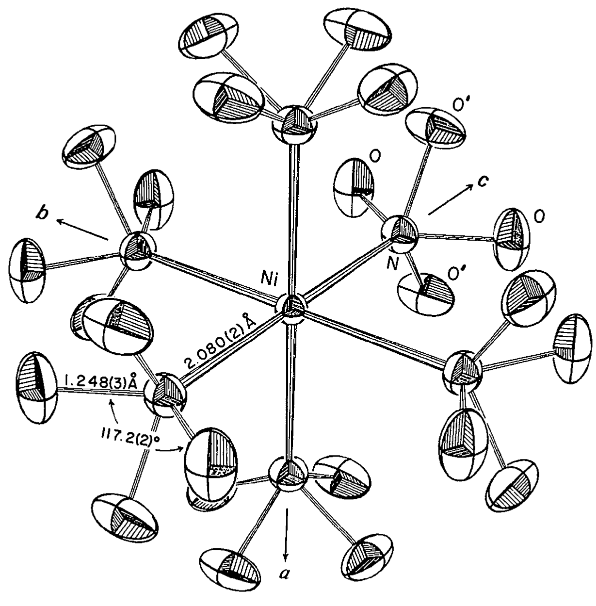

Fig. 1. Hexanitronickelate(II) anion with bond distances and angles and atomic labeling, drawn by the computer program *ORTEP* (Johnson, 1965). Thermal ellipsoids drawn at 50% probability.

Interatomic distances and angles for $K_2PbNi(NO_2)_6$ and the cubic forms of isostructural compounds with Cu(II) and Co(II) are summarized in Table 2. The tabulated results clearly show that the environments of the $Ni(NO_2)_6^{4-}$ and $Cu(NO_2)_6^{4-}$ clusters are nearly identical. This observation supports the notion that the cubic-to-orthorhombic transition results from the influence of the Jahn–Teller ions Cu(II) and Co(II).

The two sets of distances for $K_2PbCu(NO_2)_6$ given in Table 2 represent independent structure determinations. The second, carried out in our laboratory, is included because of its slightly higher precision and because refinement included an isotropic extinction correction. It provides an interesting comparison of independent structure determinations of comparable precision. No effort was made to reproduce the crystallization conditions used by Cullen & Lingafelter (1971).

The octahedral symmetry of the CuN_6 group in these cubic crystals is an apparent violation of the Jahn–Teller theorem. One explanation for this unexpected observation is the suggestion that a so-called dynamic Jahn–Teller effect is present which averages to give the CuN_6 group the octahedral symmetry seen in the X-ray experiments. In this connection, Cullen & Lingafelter (1971) note that the nitrogen atoms show greater apparent thermal motion along the Cu–N bond than at right angles to it. As shown in Table 2, our results for $K_2PbCu(NO_2)_6$ are in agreement and we further observe that in the Ni(II) crystals the thermal parameters suggest less motion along the Ni–N bond and greater motion at right angles. Since the diffraction experiment includes data to high

Table 2. *Interatomic distances and angles for selected compounds of the form* $M_2M'M''(NO_2)_6$

	$K_2PbNi(NO_2)_6$[a]	$K_2PbCu(NO_2)_6$[b]	$K_2PbCu(NO_2)_6$[c]	$K_2BaCo(NO_2)_6$[d]
M'' site symmetry	(*m*3)	(*m*3)	(*m*3)	(*m*3)
M''–N	2·080 (2) Å	2·111 (4) Å	2·118 (2) Å	1·98 (2) Å
M'–O	2·773 (2)	2·793 (3)	2·778 (1)	2·87 (2)
M—O	3·082 (1)	3·106 (1)	3·116 (1)	3·13 (1)
N—O	1·245 (2)	1·260 (4)	1·247 (2)	1·23 (2)
O—N–O	117·3 (2)°	117·9 (4)°	116·9 (2)°	114 (2)°
U_{11}	0·130 (3)	0·166 (5)	0·170 (2)	
U_{22}	0·133 (3)	0·166 (5)	0·164 (2)	
U_{33}[e]	0·115 (4)	0·198 (5)	0·182 (2)	

(*a*) This work. (*b*) Cullen & Lingafelter (1971). (*c*) Redetermination in this laboratory. Data collected in connection with cryostat checkout. Mo $K\alpha$, $2\theta_{MAX}=90°$, $R=0·012$. (*d*) Bertrand & Carpenter (1966). (*e*) U_{33} is the nitrogen-atom r.m.s. displacement in Å along the M''–N bond.

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

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Potassium Barium Hexanitronickelate(II)

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Abstract. $K_2BaNi(NO_2)_6$, cubic, $Fm3$, $a=10{\cdot}7800(4)$ Å, at 295 K ($\lambda=1{\cdot}54051$ Å), $Z=4$, $D_x=2{\cdot}918$ gcm^{-3}. Some crystals appear to have the space group $Fm3m$. An independent structure analysis has been carried out for one crystal of each type. The hexanitronickelate ion has $m3$ 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 $K_2BaNi(NO_2)_6$ 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 $Fm3$. However, some crystals from the same batch show $m3m$ Laue symmetry. This paper reports two independent structure studies of the title compound. One data set is from crystal M3 which had $m3$ Laue symmetry, the other, from crystal M3M which had $m3m$ Laue symmetry.

The true symmetry of the hexanitronickelate(II) ion is $m3$. The higher apparent symmetry ($m3m$) 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 ($84° < 2\theta < 85°$) with $\lambda=1{\cdot}54051$ 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 $K_2PbNi(NO_2)_6$ (Takagi, Joesten & Lenhert, 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 $Fm3$ and parameters obtained from $K_2PbNi(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975*b*). We soon discovered that the two crystals were not isostructural as expected and a re-examination of the $K_2BaNi(NO_2)_6$ precession films showed $m3m$ symmetry rather than the $m3$ symmetry previously seen in other cubic nitrite crystals of the

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* 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.