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Potassium and Rubidium Lead Hexanitrocobaltate(II)

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Abstract. $K_2Pb[Co(NO_2)_6]$, cubic, $Fm3$, a = 10·4853 (6) Å at 296 K ($\lambda = 0{\cdot}70926$ Å), $Z = 4$, D_x = 3·574, D_m = 3·41 Mg m^{-3}. Interatomic distances are: Co–N, 2·024 (4); Pb–O, 2·782 (3); K–O, 3·054 (2) Å. $Rb_2Pb[Co(NO_2)_6]$, cubic, $Fm3$, a = 10·6116 (8) Å at 296 K ($\lambda = 0{\cdot}63225$ Å), $Z = 4$, D_x = 3·964, D_m = 3·91 Mg m^{-3}. Interatomic distances are: Co–N, 2·046 (3); Pb–O, 2·814 (2); Rb–O, 3·096 (1) Å. The $[Co(NO_2)_6]^{4-}$ ion has $m3$ symmetry in both crystals.

Introduction. The $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$ crystal structures reported here show no departure from octahedral symmetry. This is of interest since Co^{II} in $[Co(NO_2)_6]^{4-}$ is in a low-spin d^7 configuration (Elliott, Hathaway & Slade, 1966) with the same ground state as d^9 Cu^{II}, so that a Jahn–Teller distortion is expected. Both the crystal structures and the EPR spectra of these compounds are as expected for a $[Co(NO_2)_6]^{4-}$ ion with $m3$ symmetry.

Greenish-black crystals of both $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$ were obtained by slow mixing of two solutions separated by a glass frit. For $K_2Pb[Co(NO_2)_6]$, the first solution consisted of 0·01 mol of $Co(CH_3COO)_2.4H_2O$ in 35 ml of H_2O, the second solution was 0·01 mol of $Pb(CH_3COO)_2.4H_2O$ and 0·1 mol of KNO_2 in 50 ml of H_2O. Crystals were isolated after four days. For $Rb_2Pb[Co(NO_2)_6]$, the first solution was 0·01 mol of $Co(CH_3COO)_2.4H_2O$ in 80 ml of H_2O, the second was 0·01 mol of $Pb(CH_3COO)_2.4H_2O$, 0·02 mol of $RbNO_3$ and 0·1 mol of $NaNO_2$ in 80 ml of H_2O. All solutions were purged with N_2 to prevent oxidation of Co^{II} and 10 drops of glacial acetic acid were added to prevent hydrolysis. Crystals grown by this method tended to be of irregular shape.

Precession photographs, showing $m3$ Laue symmetry and systematic absences for hkl with $h + k$, $k + l$ or $h + l$ odd, and the expected structure indicate the space group $Fm3$. The data crystals were selected from a batch of 20 to 30 crystals approximately 1 mm across which were ground slowly in an abrasion chamber for 24 to 48 h. Cell constants were determined from a least-squares fit of 2θ, ω and χ values for 14 reflections measured at both positive and negative 2θ settings on a carefully aligned diffractometer. The Mo $K\alpha_1$ line was used for $K_2Pb[Co(NO_2)_6]$ and the Mo $K\beta$ line for $Rb_2Pb[Co(NO_2)_6]$.

The densities of both crystals were measured by flotation of several crystals in a concentrated aqueous solution of thallous formate and thallous malonate. The measured density values (given in the *Abstract*) are somewhat less than those calculated from the cell constants. Since elemental analyses for nitrogen and all the cations correspond to the empirical formulae, the difference may be due to imperfections in the crystals.

Intensity data were collected using a four-circle automated diffractometer controlled by programs described previously (Lenhert, 1975). The θ–2θ scan width was 1·2° plus the 2θ-dependent dispersion factor; the number of steps was adjusted automatically so that 33 steps per degree 2θ (1 s count per step) were used for all reflections. Background was measured for 20 s at the limits of each scan. The rescan option of the control program was used to repeat the measurement of each reflection when the first scan gave $I/\sigma(I) < 20$. All reflections in the 2θ range from 11 to 90° were measured with Nb-filtered Mo $K\alpha$ radiation, those from 0 to 12° with a Y–Zr balanced filter pair.

The usual corrections were made for the Lorentz–polarization factor and for coincidence losses in the counting chain. Relative scale factors were calculated from the intensities of five monitor reflections remeasured at intervals during the data collection. Absorption corrections for the spherical crystals were based on published tables (Weber, 1969). A^* values were interpolated for μR and $1/A^*$ was fitted with a seventh-order polynomial in $\sin^2\theta$. $\bar{T}$ values for extinction corrections (Zachariasen, 1968) were approximated by a similar seventh-order polynomial. Both fits gave maximum errors of less than 0·2% and 1% for A^* and $\bar{T}$ respectively.

Both structures were refined by the full-matrix least-squares method taking as starting parameters those of cubic $K_2Pb[Cu(NO_2)_6]$. Weights for the refinement were based on counting statistics with an

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instability term of 3·0% added, as described by Miller, Lenhert & Joesten (1972). Atomic scattering factors for K^+, Rb^+, Pb^{2+}, Co^{2+}, O and N were those tabulated by Cromer & Mann (1968). Anomalous-dispersion factors for the metal ions were those given by Cromer & Liberman (1970). Computations were carried out with the XRAY 67 program (Stewart, 1967) as implemented and updated on the Vanderbilt DEC-10 computer.

Table 1. *Data-collection and refinement summary*

	$K_2Pb[Co(NO_2)_6]$	$Rb_2Pb[Co(NO_2)_6]$
Sphere size (average diameter in mm)	0·311	0·360
Maximum deviation from average	0·015	0·018
Number of reflections		
Total measured (full sphere)	9431	9714
Averaged (all $F_o > 0$)	449	464
X-ray exposure time (h)	749	814
Intensity decrease in monitor reflections (%)	5·5	2·0
Absorption correction		
Linear absorption coefficient (mm^{-1})	16·95	23·53
Absolute coefficient × radius (μR)	2·64	4·23
Maximum transmission factor	0·087	0·047
Minimum transmission factor	0·037	0·010
Final refinement cycle		
Maximum shift/error	0·012	0·001
R factor (all reflections)	0·027	0·026
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0·034	0·034
Standard error of an observation of unit weight	6·6	5·4
Final difference map		
Maximum $\Delta\rho$ near Pb^{2+} (e $Å^{-3}$)†	2·1	2·5
Minimum $\Delta\rho$ near Co^{2+} (e $Å^{-3}$)†	−6·8	−5·2
Extinction parameter (r^* in mm × 10^{-4})	0·68	0·51

† Peak values were 590 e $Å^{-3}$ for Pb^{2+} and 160 e $Å^{-3}$ for Co^{2+}.

Table 2. *Positional and thermal parameters for* $K_2Pb[Co(NO_2)_6]$ *and* $Rb_2Pb[Co(NO_2)_6]$

The anisotropic thermal parameters are of the form:

$$T = \exp[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + B_{23}klb^*c^*)].$$

$K_2Pb[Co(NO_2)_6]$

	x	*y*	*z*	*B* ($Å^2$)
K	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	3·177 (40)
Pb	0	0	$\frac{1}{2}$	1·394 (8)
Co	0	0	0	1·362 (14)
N	0	0	0·19303 (43)	
O	0·10059 (30)	0	0·25446 (29)	

	B_{11}	B_{22}	B_{33}	B_{13}
N	1·80 (11)	1·92 (11)	2·14 (12)	
O	1·80 (9)	3·86 (16)	2·49 (11)	−0·29 (7)

$Rb_2Pb[Co(NO_2)_6]$

	x	*y*	*z*	*B* ($Å^2$)
Rb	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1·999 (12)
Pb	0	0	$\frac{1}{2}$	1·353 (9)
Co	0	0	0	1·280 (15)
N	0	0	0·19282 (43)	
O	0	0·09970 (26)	0·25424 (28)	

	B_{11}	B_{22}	B_{33}	B_{23}
N	1·55 (11)	1·68 (11)	2·61 (14)	
O	2·97 (11)	1·71 (8)	3·01 (11)	−0·35 (7)

Other details of the data-collection and refinement are summarized in Table 1. The final parameters are reported in Table 2.*

Discussion. The $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$ structures reported here were selected for study to provide comparison with $K_2Ba[Co(NO_2)_6]$ and the corresponding Cu^{II} structures, $K_2Pb[Cu(NO_2)_6]$ and $Rb_2Pb[Cu(NO_2)_6]$. This research is part of a continuing effort to understand the role of the Jahn–Teller effect and of the mono- and divalent metal ions in the phase transitions of Cu^{II} and Co^{II} hexanitrite structures. We expect to find that precise structural parameters are indispensable to an understanding of the factors that affect the transition(s).

$K_2Ba[Co(NO_2)_6]$ crystallizes in the cubic phase, space group *Fm*3 (Bertrand & Carpenter, 1966), and if cooled to 263 K transforms to an orthorhombic structure, space group *Fmmm* (Bertrand, Carpenter & Kalyanaraman, 1971). $K_2Pb[Cu(NO_2)_6]$ is cubic (*Fm*3) at room temperature (Cullen & Lingafelter, 1971) and orthorhombic (*Fmmm*) below 276 K (Joesten, Takagi & Lenhert, 1977). $Rb_2Pb[Cu(NO_2)_6]$ is orthorhombic (*Fmmm*) with a transition to *Fm*3 at 306 K (Takagi, Joesten & Lenhert, 1976).

All the structures mentioned above have the same basic atomic arrangement with the metal atom of the hexanitro group at the origin, the divalent cation at $0,0,\frac{1}{2}$ and the monovalent cations at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$ as shown in Fig. 1. The hexanitro group and the divalent cation have *m*3 symmetry in the cubic phase and *mmm* symmetry in the orthorhombic phase. The hexanitro groups with *mmm* symmetry have four equal equatorial metal–nitrogen bonds with the axial bond longer (elongated configuration) or shorter (compressed

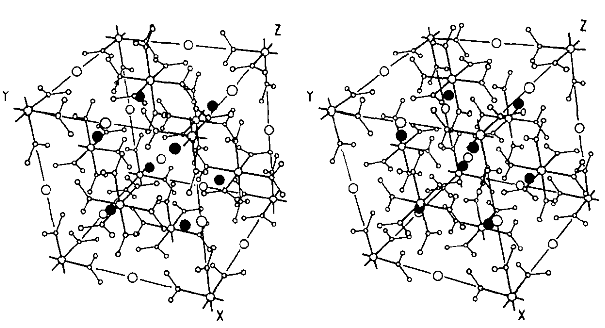

Fig. 1. *ORTEP* stereoview (Johnson, 1965) of the unit cell of $K_2Pb[Co(NO_2)_6]$. K^+ atoms are shown as solid circles, Pb^{2+} atoms as open circles along the cell edges.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35068 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

configuration). $K_2Pb[Cu(NO_2)_6]$ and $Rb_2Pb[Cu(NO_2)_6]$ are examples of the compressed case and $K_2Ba[Cu(NO_2)_6]$ is an example of the elongated configuration (Takagi, Joesten & Lenhert, 1975*a*).

Powder EPR spectra of $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$ at 296 K are isotropic as expected. The isotropic *g* values of 2·12 and 2·13 for $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$ are identical with those for cubic $K_2Pb[Cu(NO_2)_6]$ at 296 K and cubic $Rb_2Pb[Cu(NO_2)_6]$ at 319 K.

The bond distances and angles for $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$ are given in Table 3. The Rb—O distance is only 0·042 Å longer than the K—O distance even though the ionic radius is 0·15 Å larger for Rb^+ than for K^+. This suggests that the K^+ ion fits loosely in its place in $K_2Pb[Co(NO_2)_6]$ while the size of the unit cell is determined by the $Co—NO_2—Pb$ contacts. In $Rb_2Pb[Co(NO_2)_6]$ the Rb^+ ion is evidently a tight fit since the Co—N and Pb—O distances increase with no apparent reason for a change in bonding. We also note that the isotropic temperature factors for K^+ and Rb^+ (Table 2) are consistent with this view of the packing.

This picture also fits the $K_2Ba[Co(NO_2)_6]$ case where the Ba^{2+} ionic radius is nominally 0·16 Å larger than that of Pb^{2+}. The K^+ fit is very loose and the tight packing along the cell axis ($Co—NO_2—Ba$) gives a further 0·04 Å contraction in the Co—N bond (Table 3). This observation must, however, be qualified by the low precision of the $K_2Ba[Co(NO_2)_6]$ structure. A comparison of $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$ with the corresponding Cu^{II} compounds shows similar relations between the Cu—N distances and the sizes of the K^+ and Rb^+ ions. In this case the comparison is with values for $K_2Pb[Cu(NO_2)_6]$ (*Fm*3) given in Table 3 and with the average distances found in $Rb_2Pb[Cu(NO_2)_6]$ (*Fmmm*) by Takagi *et al.* (1976).

Table 3. *Interatomic distances* (Å) *and angles* (°) *for* $K_2Pb[Co(NO_2)_6]$, $Rb_2Pb[Co(NO_2)_6]$, $K_2Ba[Co(NO_2)_6]$ *and* $K_2Pb[Cu(NO_2)_6]$

	$K_2Pb[Co(NO_2)_6]$[(a)]	$Rb_2Pb[Co(NO_2)_6]$[(a)]	$K_2Ba[Co(NO_2)_6]$[(b)]	$K_2Pb[Cu(NO_2)_6]$[(c)]
Cu or Co—N	2·024 (4)	2·046 (3)	1·98 (2)	2·118 (2)
N—O	1·236 (4)	1·243 (2)	1·23 (2)	1·247 (2)
Ba or Pb—O	2·782 (3)	2·814 (2)	2·87 (2)	2·778 (1)
K or Rb—O	3·054 (2)	3·096 (1)	3·13 (1)	3·116 (1)
O—N—O	117·2 (4)	116·7 (1)	114 (2)	116·9 (2)
Co—N—O	121·4 (2)	121·7 (1)		121·6 (1)

References: (*a*) This work. (*b*) Bertrand & Carpenter (1966). (*c*) Takagi, Joesten & Lenhert (1975*b*).

The strength of the contacts between the hexanitro group and the divalent cation appears to affect the thermal-motion parameters of the N atoms. Cullen & Lingafelter (1971) observed that in $K_2Pb[Cu(NO_2)_6]$ (*Fm*3) the N atoms have larger thermal-motion parameters along the Cu—N bond than perpendicular to it. They attributed this anisotropy to a dynamic Jahn–Teller distortion. The greater thermal motion along the Co—N bond, also observed (Table 2) in $K_2Pb[Co(NO_2)_6]$ and $Rb_2Pb[Co(NO_2)_6]$, presumably has a similar cause. The thermal motion of N is, however, more nearly isotropic in $K_2Pb[Co(NO_2)_6]$ where the $Co—NO_2—Pb^{2+}$ bonds are shorter. In $Rb_2Pb[Co(NO_2)_6]$, where the spacing is greater, B_{33} for N is noticeably larger than B_{11} and B_{22}. The reduced anisotropy in $K_2Pb[Co(NO_2)_6]$ suggests that packing can modify the dynamic Jahn–Teller distortion.

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