Tableau 5. *Interactions courtes* <4 Å

Liaison	Distance *A*–*B*	Hydrogène impliqué	Distance *A*···H	Distance *B*–H	∑ des rayons de VDW des atomes *A* et *B*	∑ des rayons de VDW des atomes *A* et H
O(1)···C(5)	3,646 (4)	H(C5)	3,02 (3)	1,03 (4)	3,40	2,40
O(1)···C(6)	3,754 (4)	H(C6)	3,12 (3)	0,96 (4)	3,40	2,40
O(4)···C(2)	3,414 (4)	H(C2)	2,67 (3)	0,94 (4)	3,40	2,40
O(4)···C(3)	3,494 (4)	H(C3)	3,13 (3)	0,93 (4)	3,40	2,40
O(4)···C(5)	3,645 (4)	H(C5)	2,61 (3)	1,03 (4)	3,40	2,40
O(4)···C(8)	3,971 (4)	H′(C8)	3,56 (3)	0,98 (4)	3,40	2,40
O(5)···C(2)	3,542 (4)	H′(C2)	3,07 (3)	0,93 (4)	3,40	2,40
O(5)···C(3)	3,902 (4)	H(C3)	3,36 (3)	0,93 (4)	3,40	2,40
C(1)···C(5)	3,884 (4)	H(C5)	3,42 (3)	1,03 (4)	4,00	3,00
		H′(C5)	3,46 (3)	0,81 (4)	4,00	3,00
C(2)···C(7)	3,798 (4)	H′(C2)	3,08 (3)	0,93 (4)	4,00	3,00
		H′(C7)	3,44 (3)	1,01 (4)	4,00	3,00
C(3)···C(6)	3,746 (4)	H″(C6)	3,34 (3)	0,85 (4)	4,00	3,00
		H′(C3)	3,21 (3)	0,95 (4)	4,00	3,00
C(3)···C(8)	3,902 (4)	H(C8)	3,37 (3)	1,04 (4)	4,00	3,00
		H′(C3)	3,32 (3)	0,95 (4)	4,00	3,00
C(9)···C(5)	3,904 (4)	H(C5)	2,96 (3)	1,03 (4)	4,00	3,00

Baur, W. H. (1972). *Acta Cryst.* **19**, 909–916.

Borel, M. M., Busnot, A. & Leclaire, A. (1975*a*). *Bull. Soc. Chim. Fr.* pp. 2455–2457.

Borel, M. M., Busnot, A. & Leclaire, A. (1975*b*). *J. Inorg. Nucl. Chem.* **38**, 235–238.

Borel, M. M., Busnot, A. & Leclaire, A. (1975*c*). *J. Inorg. Nucl. Chem.* A paraître.

Borel, M. M. & Leclaire, A. (1975). *J. Inorg. Nucl. Chem.* A paraître.

Borel, M. M. & Leclaire, A. (1976). *Acta Cryst.* B**32**, 1273–1275.

Brown, G. M. & Chidambaram, R. (1973). *Acta Cryst.* B**29**, 2393–2403.

Frey, M. (1970). Thèse d'Etat, Caen.

Frey, M. & Monier, J. C. (1971). *Acta Cryst.* B**27**, 2487–2490.

Hanic, F., Stempelova, D. & Hanicova, K. (1964). *Acta Cryst.* **17**, 633–639.

Meester, P. de, Fletcher, S. R. & Skapski, A. C. (1973). *J. Chem. Soc.* pp. 2575–2578.

Morosin, B., Hughes, R. C. & Soos, Z. G. (1975). *Acta Cryst.* B**31**, 762–770.

Rollett, J. S. (1965). *Computing Methods in Crystallography*, p. 114. Oxford: Pergamon Press.

Weast, R. C. (1974). *Handbook of Chemistry and Physics*, 54th ed., *D*-157. Cleveland: C.R.C. Press.

Acta Cryst. (1976). B**32**, 1278

The Structure of Two Crystals of Rubidium Lead Hexanitrocuprate(II)

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Abstract. $Rb_2PbCu(NO_2)_6$, orthorhombic, *Fmmm*, $a=$ 10·8296 (7), $b=$ 10·8196 (7), $c=$ 10·6113 (7) Å at 295 K ($\lambda=$ 0·70926 Å), $Z=4$, $D_x=$ 3·834 g cm^{-3}. The hexanitrocuprate(II) ion is compressed along one axis. The average Cu–N distances from two independent structure determinations are 2·063 (3), 2·173 (4), and 2·173 (4) Å. A phase transition to a cubic space group is observed by e.p.r. at 317 K.

Introduction. A preliminary communication described the compressed tetragonal environment of Cu^{II} in $Rb_2PbCu(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975*a*). The present paper contains detailed structural information from two crystals for this compound at 295 K. In addition to the X-ray results we also report a phase transition from the orthorhombic form to a cubic space group, probably *Fm*3, at 317 K as observed by e.p.r.

Greenish-black crystals of $Rb_2PbCu(NO_2)_6$ were grown by slow cooling (1° h^{-1}) of a saturated solution at 50 °C (Reinen, Friebel & Reetz, 1972). Crystals of $Rb_2PbCu(NO_2)_6$, like $K_2CaCu(NO_2)_6$ (Takagi, Lenhert & Joesten, 1974) and $K_2BaCu(NO_2)_6$ (Takagi, Joesten

& Lenhert, 1975*b*), usually contain two or more lattices with one lattice more prominent than the others. Independent structure studies were carried out on two crystals each of which showed negligible diffraction from the second lattice. Systematic absences (*hkl* with $h+k$, $k+l$, or $h+l$ odd), Laue symmetry and the expected structure indicated the space group *Fmmm*, the same found for $K_2CaCu(NO_2)_6$ and $K_2BaCu(NO_2)_6$. The cell constants were determined from a least-squares refinement of 2θ, ω, and χ values for 18 Mo $K\alpha_1$ reflections ($60 < 2\theta < 65°$) for crystal 1 (cell constants for crystal 2 did not differ significantly).

Intensity data were collected for both crystals at 295 K with a four-circle automated diffractometer using diffractometer control programs developed in this laboratory (Lenhert, 1975). The general data collection conditions are described by Takagi, Joesten & Lenhert (1975*c*). Symmetry-equivalent reflections from each crystal were averaged and two sets of atomic parameters were obtained from each data set by full-matrix least-squares refinement. References for computer programs and atomic scattering factors (neutral atoms with anomalous dispersion for Pb, Cu and Rb) are given by Takagi *et al.* (1975*c*). Further details of both data collection and reduction are shown in Table 1 and/or have been described previously (Miller, Lenhert & Joesten, 1972). Refinement parameters are given in Table 1 and the final positional and thermal parameters in Table 2.*

Table 1. *Data collection and refinement summary*

	Crystal 1	Crystal 2
Crystal size (mm)	0·23 × 0·27 × 0·27	0·15 × 0·16 × 0·22
Crystal volume (mm^3)	0·0146	0·0051
Number of reflexions		
total measured	5313 ($\pm h, k, \pm l$)	5712 ($h, \pm k, \pm l$)
averaged (all $F_o > 0$)	1427	1428
X-ray exposure time (h)	105	312
Intensity decrease (%)	7	7
X-ray intensity fluct. (%)	0·867	0·84
Scan speed (deg. min^{-1})	2	1
Total bkg. time (s)	20	80
Absorption corrections		
linear abs. coef. (cm^{-1})	223·9	223·7
Gaussian integration grid	10 × 10 × 10	10 × 10 × 10
max. transmission factor	0·0823	0·1315
min. transmission factor	0·0166	0·0425
Final refinement cycle		
ave. shift/error	0·009	0·009
max. shift/error	0·158	0·077
R (all reflections)	0·026	0·027
$R_w = \{\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \sum w \lvert F_o \rvert^2\}^{1/2}$	0·029	0·026
S.E. of an observation	2·823	3·69
Final difference map		
maximum $\Delta\varrho$ (e Å^{-3}) (near Pb)	1·8	3·2
minimum $\Delta\varrho$ (e Å^{-3}) (near Pb)	−1·9	−3·3
Extinction parameter (r^*) (cm)	0·4368 × 10^{-4}	0·2101 × 10^{-4}

Discussion. $Rb_2PbCu(NO_2)_6$ is the only compound in the $M_2M'Cu(NO_2)_6$ series reported to date which has a compressed tetragonal distortion around Cu^{II} at 295 K (Takagi, Joesten & Lenhert, 1975*a*). Preliminary structural data on $K_2PbCu(NO_2)_6$ indicate a compressed tetragonal CuN_6 configuration below 281 K (Takagi *et al.*, 1974), in agreement with single-crystal e.p.r. spectra and X-ray powder data (Harrowfield & Pilbrow, 1973). A compressed tetragonal configuration

Table 2. *Positional and thermal parameters for* $Rb_2PbCu(NO_2)_6$

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}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Crystal 1									
Cu	0	0	0	1·322 (23)	1·259 (23)	0·963 (21)			
Pb	0	0	$\frac{1}{2}$	1·318 (8)	1·381 (9)	1·071 (8)			
Rb	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2·456 (18)	2·410 (18)	1·989 (16)			
O(1)	0	0·09809 (25)	0·25504 (23)	3·66 (11)	1·89 (9)	1·67 (8)	0	0	−0·34 (7)
O(2)	0·09747 (26)	0·26136 (29)	0	2·02(9)	3·75 (14)	2·93 (12)	−0·46 (9)	0	0
O(3)	0·26217 (29)	0	0·09929 (25)	4·01 (14)	3·34 (13)	1·46 (8)	0	−0·46 (9)	0
N(1)	0	0	0·19440 (34)	1·72 (12)	1·92 (14)	1·26 (11)			
N(2)	0	0·20114 (46)	0	2·39 (16)	3·03 (19)	1·47 (13)			
N(3)	0·19998 (45)	0	0	3·10 (18)	1·87 (15)	1·71 (14)			
Crystal 2									
Cu	0	0	0	1·470 (26)	1·146 (23)	1·003 (22)			
Pb	0	0	$\frac{1}{2}$	1·408 (9)	1·194 (8)	1·158 (8)			
Rb	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2·565 (20)	2·258 (18)	2·113 (17)			
O(1)	0	0·09813 (23)	0·25547 (24)	3·68 (13)	1·76 (8)	1·78 (8)	0	0	−0·41 (8)
O(2)	0·09664 (28)	0·26145 (27)	0	2·39 (11)	3·38 (13)	3·02 (12)	−0·40 (10)	0	0
O(3)	0·26195 (28)	0	0·09959 (26)	3·80 (15)	3·25 (12)	1·80 (10)	0	−0·30 (10)	0
N(1)	0	0	0·19441 (35)	1·75 (14)	1·73 (13)	1·31 (11)			
N(2)	0	0·20034 (45)	0	2·84 (20)	2·68 (18)	1·65 (14)			
N(3)	0·20117 (46)	0	0	3·12 (20)	1·72 (14)	1·55 (13)			

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* A list of structure factors of both crystals has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31544 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

has also been found in $Tl_2PbCu(NO_2)_6$ below 291 K (Harrowfield, Dempster, Freeman & Pilbrow, 1973). These structural results suggest that a compressed tetragonal environment for CuN_6 can occur when M′ is Pb.

At elevated temperatures the $Rb_2PbCu(NO_2)_6$ crystals also undergo a phase transition to a cubic space group, probably *Fm*3. This transition was reported by Reinen *et al.* (1972) who used X-ray powder diffraction but did not find a sharp transition. Single-crystal e.p.r. [using equipment and techniques described elsewhere by Joesten, Takagi & Venable (1975)] shows a sharp transition to an isotropic signal when the crystal temperature rises to 317 K. The crystal reverts from cubic to orthorhombic when the temperature is reduced to 310 K, showing a hysteresis effect consistent with the observations of Harrowfield *et al.* (1973) on $K_2PbCu(NO_2)_6$ and $Tl_2PbCu(NO_2)_6$. The cubic–orthorhombic transition temperature is related to the size of the monovalent ion (K^+, Tl^+ and Rb^+) in the $M_2PbCu(NO_2)_6$ crystals as discussed by Takagi, Joesten & Lenhert (1976).

The two independent structure determinations of $Rb_2PbCu(NO_2)_6$ presented in this paper are for crystals from separate batches. Two crystals were analyzed since we have observed differences in some crystals of $K_2BaNi(NO_2)_6$ (Takagi, Joesten & Lenhert, 1975*d*). The distances and angles for each crystal are shown in Table 3 along with average values. The $Cu(NO_2)_6^{4-}$ anion is pictured elsewhere (Takagi *et al.*, 1976).

Table 3. *Bond distances and bond angles for* $Rb_2PbCu(NO_2)_6$ *at* 295 K

	Crystal 1	Crystal 2	Average
Cu—N(1)	2·063 (4) Å	2·063 (4) Å	2·063 (3) Å
Cu—N(2)	2·176 (5)	2·169 (5)	2·173 (4)
Cu—N(3)	2·166 (5)	2·179 (5)	2·173 (4)
N(1)–O(1)	1·241 (3)	1·244 (3)	1·243 (2)
N(2)–O(2)	1·241 (4)	1·238 (4)	1·240 (3)
N(3)–O(3)	1·250 (4)	1·245 (4)	1·248 (3)
Pb—O(1)	2·808 (3)	2·804 (3)	2·806 (2)
Pb—O(2)	2·789 (3)	2·786 (3)	2·788 (2)
Pb—O(3)	2·783 (3)	2·787 (3)	2·785 (2)
Rb—O(1)	3·168 (1)	3·169 (1)	3·169 (1)
Rb—O(2)	3·127 (1)	3·133 (2)	3·130 (1)
Rb—O(3)	3·145 (1)	3·145 (1)	3·145 (1)
O(1)–N(1)–O(1)	117·5 (4)°	117·2 (4)°	117·4 (3)°
O(2)–N(2)–O(2)	116·6 (6)	115·4 (6)	116·0 (4)
O(3)–N(3)–O(3)	114·8 (6)	116·2 (6)	115·5 (4)
Cu—N(1)–O(1)	121·2 (2)	121·4 (2)	121·3 (2)
Cu—N(2)–O(2)	121·7 (2)	122·3 (2)	122·0 (2)
Cu—N(3)–O(3)	122·6 (2)	121·9 (2)	122·3 (2)

A half-normal probability plot analysis (Abrahams & Keve, 1971) of the observed *versus* expected parameter differences from Table 2 shows a broken line. If the nine refined coordinates are plotted separately a straight line with a slope slightly greater than unity is obtained. A similar plot of temperature factors has a slope of about 7, suggesting either a systematic error in the data or a difference in the two crystals.* The heavy-atom thermal motion in crystal 1 is uniformly larger along **b** and smaller along **a** and **c** with a similar trend for the nitro groups. X-ray absorption is large for both crystals (see Table 1) and small errors in the crystal measurements used for the absorption correction could easily lead to the observed half-normal probability plot. Since the coordinates of the two crystals are in agreement, we find no evidence of variation in crystals of $Rb_2PbCu(NO_2)_6$ as measured by bond distances and angles but the analysis also demonstrates the unreliability of thermal motion parameters, especially in highly absorbing crystals.

The thermal motion of the nitrogen atoms (Table 2) has an interesting feature which appears in both crystals. N(1), the participant in the short Cu–N bond, has its maximum vibration perpendicular to the Cu–N bond. Both N(2) and N(3) which are involved in the longer Cu–N bonds show greater amplitude along the Cu–N bond. A similar apparent thermal motion along the Cu–N bond has been noted by Cullen & Lingafelter (1971) in cubic $K_2PbCu(NO_2)_6$ and confirmed by us in independent structure analysis (Takagi *et al.*, 1975*c*). In this case it has been interpreted as evidence for a dynamic Jahn–Teller distortion which is 'frozen out' to give the compressed tetragonal CuN_6 configuration when the temperature of the crystals is reduced to 281 K.

In $Rb_2PbCu(NO_2)_6$ the long Cu–N bonds are 2·173 Å, almost exactly equal to the average of 2·050 and 2·313 Å found for $K_2CaCu(NO_2)_6$, a typical elongated tetragonal CuN_6 configuration (Takagi *et al.*, 1974). This led us to wonder if the apparent compressed configuration might result from an averaging of two elongated CuN_6 configurations so that one long and one short bond coincided and the other short bond (the 2·063 Å bond) maintained a constant orientation. However, no change in the crystal lattice is observed when the $Rb_2PbCu(NO_2)_6$ crystals are cooled to 130 K as would be expected if the observed compressed tetragonal CuN_6 configuration resulted from a dynamic averaging effect.

We have previously shown that crystals of the $M_2M'Ni(NO_2)_6$ series are isostructural with the cubic Cu^{II} series and retain their cubic symmetry down to 130 K (Takagi *et al.*, 1975*c*). This observation together with the present structure results provides additional experimental evidence that in the $M_2M'Cu(NO_2)_6$ compounds the counter ions M and M′ control the type of Jahn–Teller distortion (compressed or elongated tetragonal) of the CuN_6 group as well as the temperature of transition from the dynamic to the static phase. However, it is not clear why Pb^{II} gives a compressed tetragonal CuN_6 environment in the static phase while Ca^{II}, Ba^{II} and Sr^{II} all give an elongated tetragonal CuN_6 environment (Takagi *et al.*, 1974, 1975*b*, *e*).

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* These plots have been deposited along with the structure factors.

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References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

Cullen, D. L. & Lingafelter, E. C. (1971). *Inorg. Chem.* **10**, 1264–1268.

Harrowfield, B. V., Dempster, A. J., Freeman, T. E. & Pilbrow, J. R. (1973). *J. Phys. (C): Solid State Phys.* **6**, 2058–2065.

Harrowfield, B. V. & Pilbrow, J. R. (1973). *J. Phys. (C): Solid State Phys.* **6**, 755–766.

Joesten, M. D., Takagi, S. & Venable, J. H. (1975). *Chem. Phys. Lett.* **36**, 536–538.

Lenhert, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.

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.

Takagi, S., Joesten, M. D. & Lenhert, P. G. (1975*a*). *J. Amer. Chem. Soc.* **97**, 444–445.

Takagi, S., Joesten, M. D. & Lenhert, P. G. (1975*b*). *Acta Cryst.* B**31**, 596–598.

Takagi, S., Joesten, M. D. & Lenhert, P. G. (1975*c*). *Acta Cryst.* B**31**, 1968–1970.

Takagi, S., Joesten, M. D. & Lenhert, P. G. (1975*d*). *Acta Cryst.* B**31**, 1970–1972.

Takagi, S., Joesten, M. D. & Lenhert, P. G. (1975*e*). Unpublished results.

Takagi, S., Joesten, M. D. & Lenhert, P. G. (1976). *Acta Cryst.* B**32**, 326–328.

Takagi, S., Lenhert, P. G. & Joesten, M. D. (1974). *J. Amer. Chem. Soc.* **96**, 6606–6609.

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Tetraaquobis(succinimidato)nickel(II) Dihydrate

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Abstract. Orthorhombic, *Pnnm*, $a=8{\cdot}6580$ (8), $b=7{\cdot}1118$ (8), $c=12{\cdot}522$ (1) Å, $C_8H_8N_2O_2Ni.6H_2O$, $Z=2$, $D_m=1{\cdot}57$, $D_c=1{\cdot}563$ g cm^{-3}. Two of the coordinated water molecules form intramolecular hydrogen bonds to the carbonyl O atoms, whereas the other two are involved with water of crystallization in intermolecular bonding.

Introduction. Pale blue prismatic crystals were prepared as previously described (Ley & Werner, 1906). Mean weight loss on heating, 29·7%; calculated for $6H_2O$ per molecule of complex, 29·8%. Data were collected using a Hilger–Watts automated diffractometer, Mo $K\alpha$ radiation, to a θ limit of 33°, giving a set of 481 observed data. Systematic absences were in $hk0$ when $h+k$ odd, $0kl$ when $k+l$ odd. Space group *Pnnm* was assumed, and no feature of the structure gave cause to doubt it. The Ni atom position was fixed by symmetry, and all non-hydrogen atoms were readily placed from the heavy-atom phased density synthesis. H atoms were subsequently located from difference syntheses. Refinement was by full-matrix least squares, minimizing $\sum w(F_o-F_c)^2$, with weights based on the relationship $\sigma(I)=[\sigma^2(c)+(0{\cdot}04I)^2]^{1/2}$ where $\sigma^2(c)$ is the variance from counting statistics. Anisotropic thermal parameters were adopted, except for the H atoms which were given a constant isotropic parameter of 5·0 Å^2. The final R was 0·043. A final difference synthesis confirmed that no atom had been overlooked. Atom coordinates and thermal parameters are listed in Table 1,

Table 1. *Atomic coordinates and temperature factors*

	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	0·0089 (2)	0·0180 (3)	0·0033 (1)	−0·0005 (4)	0	0
N	0	0	0·1679 (3)	0·0082 (6)	0·017 (1)	0·0028 (3)	−0·0000 (20)	0	0
O	0·2565 (4)	−0·0555 (6)	0·1974 (3)	0·0099 (5)	0·037 (1)	0·0042 (2)	0·0018 (7)	−0·0010 (3)	−0·0014 (4)
C(1)	0·1257 (6)	−0·0270 (9)	0·2317 (3)	0·0111 (7)	0·019 (2)	0·0036 (2)	−0·0011 (9)	−0·0000 (3)	0·0007 (6)
C(2)	0·0853 (7)	−0·0165 (14)	0·3484 (3)	0·0152 (8)	0·029 (2)	0·0029 (2)	0·0004 (17)	−0·0008 (4)	0·0012 (8)
O(*W*1)	0·2332 (7)	0·0898 (9)	0	0·0105 (8)	0·024 (2)	0·0056 (4)	−0·0048 (9)	0	0
O(*W*2)	−0·0820 (7)	0·2712 (7)	0	0·0132 (8)	0·015 (1)	0·0040 (3)	−0·0014 (8)	0	0
O(*W*3)	0	0·5	0·1685 (3)	0·0105 (6)	0·023 (1)	0·0035 (3)	0·0010 (17)	0	0
H(C1)	0·120 (7)	−0·137 (9)	0·392 (4)	5·0					
H(C2)	0·164 (7)	0·076 (8)	0·386 (4)	5·0					
H(*W*1)	0·272 (7)	0·036 (9)	0·053 (4)	5·0					
H(*W*2)	0·452 (6)	0·149 (8)	0·441 (4)	5·0					
H(*W*3)	0·085 (6)	0·464 (9)	0·200 (4)	5·0					