Potassium Barium Hexanitrocuprate(II) at 295 K

By Shozo Takagi and Melvin D. Joesten

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

and P. Galen Lenhert

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

Abstract. $K_2BaCu(NO_2)_6$, orthorhombic, *Fmmm*, $a =$ 11·219 (2), $b = 10·728$ (2), $c = 10·685$ (1) Å at 295 K ($\lambda = 0·70926$ Å), $Z = 4$, $D_m = 2·871$, $D_c = 2·867$ g cm^{-3}. $K_2BaCu(NO_2)_6$ is isomorphous with $K_2CaCu(NO_2)_6$ but not with $K_2PbCu(NO_2)_6$. The hexanitrocuprate(II) ion is elongated along one axis to give Cu–N distances of 2·311 (2), 2·048 (2) and 2·038 (2) Å.

Introduction. Crystals of $K_2BaCu(NO_2)_6$ were obtained by the method of Elliott, Hathaway & Slade (1966) with the substitution of copper(II) nitrate for copper(II) acetate. Crystals of $K_2BaCu(NO_2)_6$, like $K_2CaCu(NO_2)_6$, usually contain two or more lattices with one lattice more prominent than the other (Takagi, Lenhert & Joesten, 1974). Systematic absences (*hkl* with $h+k$, $k+l$, or $h+l$ odd) and the expected structure indicate the space group to be *Fmmm*, which is confirmed by the successful refinement.

The crystal used for data collection measured about $0·18 \times 0·19 \times 0·34$ mm, had a volume of $0·0110$ mm^3, and showed negligible diffraction from the second lattice. The cell constants given above were determined from the least-squares refinement of 2θ, ω, and χ values for 18 Mo $K\alpha_1$ reflections ($55 < 2\theta < 65°$). A four-circle automated diffractometer was used to collect intensity data at 295 K for all 1470 independent reflections out to $2\theta = 90°$ (Nb-filtered Mo $K\alpha$ radiation with θ–2θ scans at 1° min^{-1}). All but one reflection were observed ($F_o > 0$). Three monitor reflections showed a slow intensity decrease of about 9% during the data collection. Absorption corrections were made with the computer program *ORABS* (Wehe, Busing & Levy, 1972), using a linear absorption coefficient for Mo $K\alpha$ of 55·64 cm^{-1}; maximum and minimum transmission factors were 0·440 and 0·345. Further details of the data collection and reduction methods have been described previously (Miller, Lenhert & Joesten, 1972).

The crystal structure of $K_2BaCu(NO_2)_6$ was refined by using, as starting coordinates, those obtained for the isostructural $K_2CaCu(NO_2)_6$. All atoms were refined anisotropically along with an isotropic extinction parameter which refined to a value of $0·1033 \times 10^{-4}$ cm for r^* (Zachariasen, 1968). The final positional and thermal parameters are given in Table 1.

The full-matrix least-squares refinement on F with all 1470 reflections gave a conventional R of 0·016.† The final average and maximum shift-to-error ratios for the atomic parameters are 0·01 and 0·15, respectively. A final difference map showed maximum density of 0·5 e Å^{-3} and minimum values of about $-1·0$ e Å^{-3} near the Ba and Cu ions. The least-squares weights were based on counting statistics and included the usual instability term with a value of 1·113% (Miller *et al.*, 1972). The resulting standard error of an observation of unit weight was 2·73. 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.

Atomic scattering factors for all atoms were those tabulated by Cromer & Mann (1968). The ionized forms

---

Table 1. *Positional and thermal parameters for* $K_2BaCu(NO_2)_6$

The thermal parameters are of the form $T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
No standard deviations are given for parameters fixed by crystal symmetry.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	1·451 (13)	1·007 (11)	0·900 (11)	0	0	0
Ba	0	0	½	1·180 (6)	1·043 (6)	1·001 (6)	0	0	0
K	¼	¼	¼	4·43 (5)	3·83 (5)	3·91 (5)	0	0	0
O(1)	0·0940 (2)	¼	0·2505 (1)	2·02 (5)	4·58 (10)	1·42 (4)	0	−0·25 (4)	0
O(2)	0·2643 (1)	0·0977 (2)	0	1·84 (6)	1·82 (5)	5·03 (11)	−0·09 (4)	0	0
O(3)	0	0·2505 (1)	0·0982 (2)	5·63 (12)	1·49 (5)	1·65 (5)	0	0	−0·30 (4)
N(1)	0	0	0·1908 (2)	1·95 (7)	1·68 (7)	1·18 (6)	0	0	0
N(2)	0·2060 (2)	0	0	1·50 (7)	1·97 (8)	2·19 (8)	0	0	0
N(3)	0	0·1909 (2)	0	2·15 (8)	1·15 (6)	1·59 (7)	0	0	0

for Cu^{2+}, Ba^{2+} and K^+ were used. Anomalous scattering factors were given by Cromer & Liberman (1970).

Discussion. The $K_2BaCu(NO_2)_6$ structure reported here is one of a series of Cu and Ni nitrite compounds under study in this laboratory. The objective of the study is to describe the Cu coordination and elucidate those factors which contribute to cubic, to compressed tetragonal, and to elongated tetragonal $Cu(NO_2)_6$ coordination.

The hexanitrocuprate(II) anion (Fig. 1) assumes the elongated configuration in both $K_2BaCu(NO_2)_6$ and in the previously reported $K_2CaCu(NO_2)_6$ (Takagi et al., 1974). Bond distances and angles for both of these compounds are compared in Table 2. The Cu–N
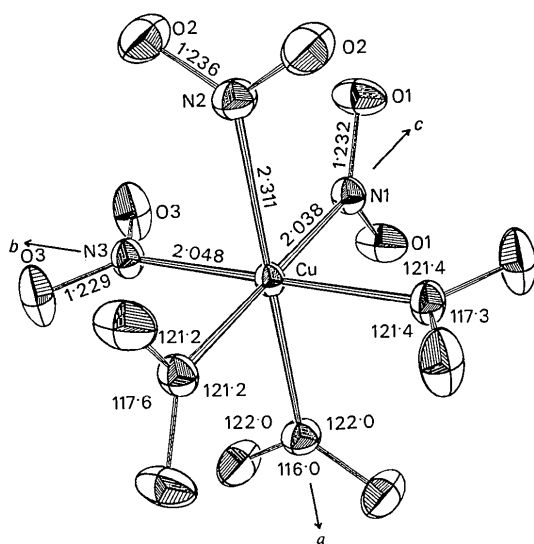

Fig. 1. Hexanitrocuprate(II) anion with bond distances and angles and atomic numbering, drawn by the computer program ORTEP (Johnson, 1965).
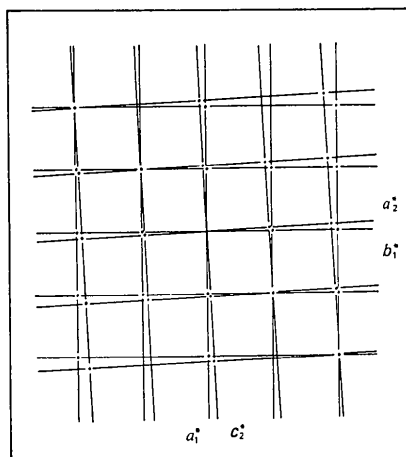

Fig. 2. Schematic drawing of zero-layer precession photograph of $K_2BaCu(NO_2)_6$ at 295 K. The drawing is based on an actual precession photograph of a twinned crystal.

distances are little affected by the substitution of Ba^{2+} for Ca^{2+} although it appears that the departure from tetragonal symmetry for CuN_6 in the Ba^{2+} crystals may be real. The distances and angles in the NO_2 ligands appear to differ slightly when the nitrite groups with long and short Cu–N distances are compared. The differences are statistically significant in both the Ca^{2+} and Ba^{2+} environments but we offer no explanation for the observed decrease of about 1·4° in the O–N–O angle and an increase of about 0·006 Å in the N–O bond in the distant ligand as compared to the close one.

Table 2. *Comparison of bond distances and angles for* $K_2BaCu(NO_2)_6$ *and* $K_2CaCu(NO_2)_6$

Standard deviations are given in parentheses.

	$K_2BaCu(NO_2)$ *		$K_2CaCu(NO_2)$ †
Cu—N(1)	2·038 (2) Å		2·050 (1) Å
Cu—N(2)	2·311 (2)		2 313 (1)
Cu—N(3)	2·048 (2)		2·052 (1)
N(1)–O(1)	1·232 (2)		1·246 (1)
N(2)–O(2)	1·236 (2)		1·252 (1)
N(3)–O(3)	1·229 (2)		1·246 (1)
Ba—O(1)	2·866 (1)	Ca–O(1)	2·674 (1)
Ba—O(2)	2·844 (2)	Ca–O(2)	2·610 (1)
Ba—O(3)	2·875 (2)	Ca–O(3)	2·676 (1)
K—O(1)	3·203 (1)		3·053 (1)
K—O(2)	3·135 (1)		3·011 (1)
K—O(3)	3·240 (1)		3·088 (1)
O(1)–N(1)–O(1)	117·6 (2)°		116·6 (1)°
O(2)–N(2)–O(2)	116·0 (2)		115·2 (1)
O(3)–N(3)–O(3)	117·3 (2)		116·7 (1)

* This work.
† Takagi, Lenhert & Joesten (1974).

The tendency of both $K_2BaCu(NO_2)_6$ and $K_2CaCu(NO_2)_6$ to crystallize as twins has discouraged attempts at structure determination, but careful selection of crystals with negligible diffraction from a second lattice leads to a result of very acceptable accuracy for both the barium salt ($R=0·016$) and the calcium salt ($R=0·032$). The observed twinning (Fig. 2) is in accord with the notion that a dynamic Jahn–Teller distortion can be trapped in a favorable crystal field. A similar twinning occurs in the $K_2PbCu(NO_2)_6$ structure which is cubic ($Fm3$) and single at room temperature but undergoes a phase transition to an orthorhombic cell ($Fmmm$) on cooling to about 7 °C. The low-temperature form is twinned and the transition has been studied by Harrowfield & Pilbrow (1973).

In $K_2BaCu(NO_2)_6$ the twinning is such that the first lattice can be brought into coincidence with the second by a 90° rotation about **a** (**b** into **c**) followed by a 92·8° rotation about the new direction of **b** (**c** into **a**). Thus **a** → **c**, **b** → **a**, and **c** → **b**, approximately. The schematic drawing of the zero layer precession photograph (Fig. 2) illustrates the {110} boundary which the two lattices share. A further discussion of the twinning and its relation to the observed phase transition in the $K_2PbCu(NO_2)_6$ crystals will be published in a future paper.

The effect of counter ions on the symmetry of $Cu(NO_2)_6^{4-}$ is puzzling. We have shown that K_2Ba^{4+} and K_2Ca^{4+} give an *elongated* tetragonal environment around Cu^{II} at 295°K. However, preliminary results indicate that K_2Pb^{4+} and Rb_2Pb^{4+} give a *compressed* tetragonal distortion below 280 and at 295 K, respectively.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

ELLIOTT, H., HATHAWAY, B. J. & SLADE, R. C. (1966). *Inorg. Chem.* 5, 669–677.

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.

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., 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, a Fortran Program for Calculating Single-Crystal Absorption Corrections*. Oak Ridge National Laboratory Report ORNL-TM-229.

ZACHARIASEN, W. H. (1968). *Acta Cryst.* A24, 212–216.

1,2-Diphenylethanesilver(I) Perchlorate

BY I. F. TAYLOR JR AND E. L. AMMA*

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, *U.S.A.*

Abstract. $[(C_6H_5)_2(CH_2)_2]Ag^I ClO_4$, orthorhombic, *Pbnm*, $Z=4$, M.W. 389·5, $a=5\cdot871$ (1), $b=12\cdot575$ (2), $c=18\cdot731$ (3) Å, $D_x=1\cdot87$, $D_m=1\cdot7$–$2\cdot1$ g cm^{-3} (by flotation), $\lambda(Mo\ K\alpha)=0\cdot71068$ Å, $\mu(Mo\ K\alpha)=16\cdot2$ cm^{-1}, R(final)$=0\cdot076$. The Ag atom is disordered in such a way that some Ag's have square-pyramidal and others have square-planar coordination geometry from bonding to oxygen of perchlorate and π-bonding to benzene.

Introduction. As part of a program examining the interaction between Ag^I and aromatic hydrocarbons (Griffith & Amma, 1971), we synthesized the title compound by reacting anhydrous $AgClO_4$ and 1,2-diphenylethane (DPE) in toluene. Diffraction quality crystals were grown by slow evaporation of the solution and sealed in thin-walled glass capillaries for X-ray studies. Weissenberg and precession photographs $hk0\cdots hk7$, $h0l$, $0kl$ revealed orthorhombic symmetry and the extinctions $0kl$, $k=2n+1$ and $h0l$, $h+l=2n+1$, establishing the possible space group as *Pbnm* or *Pbn2₁*. The correct choice of space group was *Pbnm* as shown by the structure analysis. A least-squares treatment of χ, φ, ω and 2θ values of 20 well centered

reflections gave the cell dimensions: $a=5\cdot871$; $b=12\cdot575$ (2); $c=18\cdot731$ (3) Å; $\lambda=0\cdot71068$ Å. The density was only bracketed between the values 1·70 and 2·10 g cm^{-3} since the crystals disintegrated in solvents of appropriate density. Assuming four molecules per cell the calculated density is 1·87 g cm^{-3}. A crystal with dimensions $0\cdot20 \times 0\cdot20 \times 1\cdot0$ mm was mounted such that the long direction (c) was approximately parallel to the φ axis. Reflections were measured by a θ–2θ scan technique with Zr-filtered Mo $K\alpha$ radiation and a scan time of 81 s at a rate of 0·0333° s^{-1}, and the backgrounds were counted at $\pm1\cdot35°$ 2θ of peak maximum for 20 s. The counting rate never exceeded 5000 c s^{-1}. After every ten reflections a standard peak was measured to monitor stability of electronics, crystal decomposition and alignment. (A peak of average intensity approximately in the center of the χ, φ, 2θ range was chosen for maximum sensitivity.) The variation of the standard peak was σ or less throughout the data collection where $\sigma(I)=[I_{scan}+(2\cdot025)^2(B_1+B_2)]^{1/2}$. Reflections were considered absent if the integrated intensity was less than $2[(2\cdot025)^2(B_1+B_2)]^{1/2}$, ($2\sigma$ of background). From the approximately 1400 reflections measured, 447 were considered nonzero by the above criterion. (The disorder found for the Ag atoms is, no doubt, the reason for the abbrevi-

---

* Address all correspondence to this author.