Structure of Potassium Calcium Hexanitrocuprate(II) at 295°K. Evidence for a Static Jahn-Teller Distortion

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Abstract: Crystals of potassium calcium hexanitrocuprate(II), $K_2CaCu(NO_2)_6$, usually have two or more orthorhombic lattices, space group *Fmmm*, with identical unit cells containing four formula units ($a = 10.743$ (3), $b = 10.325$ (2), $c = 10.318$ (2) Å). Data collected from a crystal with two lattices were used to solve and refine each of the two crystal structures which showed identical hexanitrocuprate(II) ions with different orientations. A more precise result was obtained from a crystal showing negligible diffraction from subsidiary lattices. These data (four-circle diffractometer, 2θ scan, Mo Kα radiation $0 < 2\theta < 90°$, 1310 independent reflections) were refined by full-matrix least squares to $R = 0.032$. The CuN_6 group has tetragonal symmetry with Cu-N distances of 2.313 (1), 2.052 (1), and 2.050 (1) Å. This structure is compared with preliminary results for orthorhombic $K_2PbCu(NO_2)_6$ at 193°K (cell dimensions of $a = 10.72$ (1), $b = 10.74$ (1), $c = 10.51$ (1) Å) which suggest the presence of a compressed tetragonal distortion. These results from $K_2CaCu(NO_2)_6$ at 295°K and $K_2PbCu(NO_2)_6$ at 193°K provide direct experimental evidence for the static-dynamic Jahn-Teller distortion.

The high symmetry of Cu(II) in tris(octamethylpyrophosphoramide)copper(II) perchlorate,[2] potassium lead hexanitrocuprate(II),[3] and tris(ethylenediamine)copper(II) sulfate[4] has been attributed to a dynamic Jahn-Teller effect. Low temperature X-ray[5] and epr results[6] for the first compound are consistent with the dynamic-static Jahn-Teller theory proposed by Abragam and Pryce.[7,8] This theory assumes the presence of three mutually perpendicular tetragonal distortions of equal energy. Rapid oscillation among the three distortions gives an average structure with high symmetry, but at low temperatures static distortions appear. The transition temperature depends on the compound.

We are studying several of these compounds by X-ray crystallography at temperatures where the static distortions are present in order to provide experimental data on the magnitude and direction of distortions which are attributable to the Jahn-Teller effect. Systems which appear to be undergoing a dynamic-static Jahn-Teller effect are ideal since other factors which may cause distortions are either not present or negligible.[9] A recent report[10] on the low temperature X-ray study of the static distortion around Co(II) in the strong field environment of $K_2BaCo(NO_2)_6$ indicates the feasibility of this approach.

Complete structure determinations for the series $K_2MCu(NO_2)_6$ where M is Pb, Ba, or Ca are particularly appropriate for several reasons. X-Ray powder data[11] have shown that the symmetry of the unit cell of

$K_2PbCu(NO_2)_6$ is lowered either by replacing Pb(II) with Ca(II) or with Ba(II) or by lowering the temperature. Hathaway, Dudley, and Nicholls[12] have predicted an elongated tetragonal environment for Cu(II) in the barium salt on the basis of single-crystal polarized electronic spectra and unit cell parameters. However, Harrowfield and Pilbrow[13] have interpreted single-crystal epr studies of $K_2PbCu(NO_2)_6$ below 280°K in terms of tetragonally *compressed* environment for Cu(II). Since the corresponding $K_2MNi(NO_2)_6$ series is cubic for M = Ca, Ba, or Pb,[11,14] the differences observed for the $K_2MCu(NO_2)_6$ series must be due to Jahn-Teller effects.

Complete structure information on $K_2Ca(NO_2)_6$ and $K_2BaCu(NO_2)_6$ at room temperature and $K_2PbCu(NO_2)_6$ at low temperature would verify the type of distortion and provide information on the magnitude of the distortion. The present paper is a report of the potassium calcium hexanitrocuprate(II) structure at 295°K.

Experimental Section

Greenish black crystals of $K_2CaCu(NO_2)_6$ were obtained by the method of Elliott, Hathaway, and Slade[11] with the substitution of copper(II) nitrate for copper(II) acetate. Photographs of several different crystals at room temperature showed two or more lattices with one usually more prominent than the others. When two lattices are about equally prominent, we observe that they represent identical unit cells but with one lattice rotated from the other. The first lattice can be brought into coincidence with the second by a 90° rotation about a (b into c) followed by a 92.2° rotation about the new direction of b (c into a). Thus $a \rightarrow c$, $b \rightarrow a$, and $c \rightarrow b$, approximately. Crystals which contain more than one lattice are not transparent.

Precession photographs showing systematic absences for *hkl* with $h + k$, $k + l$, or $h + l$ odd indicated one of three orthorhombic space groups: *Fmmm*, *Fmm2*, and *F222*.[15] The space group *Fmmm* was assumed and the successful refinement of the structure confirms that choice.

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Table I. Parameters for K₂CaCu(NO₂)₆[a,b]

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	1.251 (9)	0.865 (8)	0.829 (8)	0	0	0
Ca	0	0	$^1/_2$	1.176 (13)	1.104 (13)	1.160 (12)	0	0	0
K	$^1/_4$	$^1/_4$	$^1/_4$	2.484 (14)	2.208 (13)	2.342 (12)	0	0	0
O(1)	0.09870 (8)	0	0.26213 (8)	1.78 (3)	2.50 (3)	1.65 (3)	0	−0.46 (2)	0
O(2)	0.27782 (8)	0.10235 (8)	0	1.96 (3)	1.54 (3)	2.68 (3)	−0.28 (3)	0	0
O(3)	0	0.26211 (8)	0.10281 (7)	2.88 (4)	1.55 (3)	1.43 (2)	0	0	−0.35 (2)
N(1)	0	0	0.19871 (11)	1.54 (4)	1.14 (4)	1.18 (4)	0	0	0
N(2)	0.21533 (13)	0	0	1.38 (4)	1.59 (4)	1.55 (4)	0	0	0
N(3)	0	0.19874 (12)	0	1.34 (4)	1.14 (4)	1.30 (4)	0	0	0

[a] No standard deviations are given for parameters fixed by crystal symmetry. [b] The anisotropic temperature factors are in the form $T = \exp[-^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Preliminary intensity data were collected using a crystal with two prominent lattices. A narrow receiving aperture and ω scans were used to largely eliminate reflections from the other lattice. The structure was solved by a consideration of the expected molecular structure, the symmetry and multiplicity of the special positions in *Fmmm*, and reference to a sharpened three-dimensional Patterson function. The two data sets, one from each lattice, each consisting of about 300 independent reflections, were refined independently by the least-squares method using isotropic thermal parameters. The result indicated two identical crystal structures each with one long pair of Cu–N distances and two short pairs equal within estimated error. One structure was rotated 92.2° from the other as described above. Both data sets refined to an R value of about 0.08.

Eventually a partially transparent crystal was found, and precession photographs showed negligible diffraction from the second lattice. The habit corresponded approximately to cubic symmetry with the {100} and {111} forms prominently developed. It measured 0.17 × 0.15 × 0.14 mm and was mounted with a^* parallel to the ϕ axis of the diffractometer.

Cell parameters were determined at 22° from 11 reflections (25 < 2θ < 35°) centered automatically on the computer-controlled diffractometer using Mo Kα radiation (λ 0.7107 Å). The cell constants and three orientation parameters were obtained by least-squares fit of the 2θ, ω, and χ observations which gave $a = 10.743$ (3), $b = 10.325$ (2), and $c = 10.318$ (2) Å. The crystal density of 2.655 g/cm³, measured by flotation in a mixture of ethylene dichloride and tetrabromoethane, compares with the calculated value of 2.657 g/cm³ based on four molecules per unit cell (volume 1144.5 Å³) and a molecular weight of 457.85 daltons.

Three-dimensional intensity data were collected at 22° with a Picker four-circle automated diffractometer (FACS-I system) using a Digital Equipment Corp. PDP-8/I with auxiliary disk memory. The diffractometer control program, based on the Picker FACS-I programs, was extensively modified and adapted for use with the disk memory in this laboratory.[16] Data collection conditions described previously[17] were used with minor modifications.

All reflections (except space group extinctions) out to 2θ = 90° in the *hkl* and *hkl̄* octants were measured once and then combined to give a total of 1310 independent reflections including 1280 with $F_o > 0$. Three standard reflections, measured every 80 reflections to monitor X-ray source and detector stability, showed a slow intensity decrease of about 10% during the data collection.

The data were reduced in the usual manner as described by Miller, Lenhert, and Joesten.[17] Absorption corrections using a linear absorption coefficient calculated from mass absorption coefficients for Mo Kα[18] of 32.1 cm⁻¹ gave maximum and minimum transmission factors of 0.685 and 0.622, respectively.

The crystal structure of K₂CaCu(NO₂)₆ was refined by using the coordinates obtained from the preliminary data of the 2-lattice crystal. In the space group, *Fmmm*, the four copper atoms occupy the special position a (*mmm* symmetry) and the four calcium atoms, b (*mmm*). Special position f (222) is occupied by eight potassium atoms, g, h, and i (*mm*) are occupied by 24 nitrogen atoms, and m, n, and o (*m*) are occupied by 48 oxygen atoms.

The structure was refined by the full-matrix least-squares technique by minimizing $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. All atoms were refined anisotropically along with the extinction param-

eters which refined to a value of 0.0487 × 10⁻⁴ cm for r^* (Zachariasen[19]).

Atomic scattering factors for Cu(II), O, and N were those tabulated by Cromer and Mann.[20] The values for Ca(II) and K(I) were taken from the "International Tables for X-Ray Crystallography."[18] Anomalous scattering factors were those given by Cromer and Liberman.[21]

The final cycles of full-matrix least squares, including all 1310 reflections, reduced the conventional R factor, $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, to 0.032, and the weighted R factor, $R_w = \{[(\Sigma w|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{1/2}$ to 0.022. The final error in an observation of unit weight was 1.94 and the final average and maximum shift-to-error ratios for the atomic parameters were 0.02 and 0.16, respectively. The final positional and thermal parameters and their standard deviations are displayed in Table I. The values shown were used (before rounding) in the calculation of the final structure factors.[22]

Structure factor, electron density, bond distance–angle, and least-squares calculations were carried out with the X-Ray 67 programs[23] as implemented and updated on the Vanderbilt Sigma 7 Computer.

Description and Discussion of the Structure

The hexanitrocuprate(II) anion is shown alone in Figure 1a and with nearest neighbor cations, Ca(II) and K(I), in Figure 1b. Bond distances and angles are shown in Table II and in Figure 1. The standard

Table II. Comparison of Bond Distances (Å) and Angles (deg) for K₂CaCu(NO₂)₆ and K₂PbCu(NO₂)₆[a]

	K₂CaCu(NO₂)₆	K₂PbCu(NO₂)₆
Cu–N(1)	2.050 (1)[b]	2.111 (4)[b]
Cu–N(2)	2.313 (1)	
Cu–N(3)	2.052 (1)	
N(1)–O(1)	1.246 (1)	1.260 (4)
N(2)–O(2)	1.252 (1)	
N(3)–O(3)	1.246 (1)	
Ca–O(1) or Pb–O	2.674 (1) Pb–O	2.793 (3)
Ca–O(2)	2.610 (1)	
Ca–O(3)	2.676 (1)	
K–O(1)	3.053 (1)	3.106 (1)
K–O(2)	3.011 (1)	
K–O(3)	3.088 (1)	
O(1)–N(1)–O(1)	116.6 (1)	117.9 (4)
O(2)–N(2)–O(2)	115.2 (1)	
O(3)–N(3)–O(3)	116.7 (1)	

[a] Reference 3. [b] Standard deviations of the last significant figure are given in parentheses.

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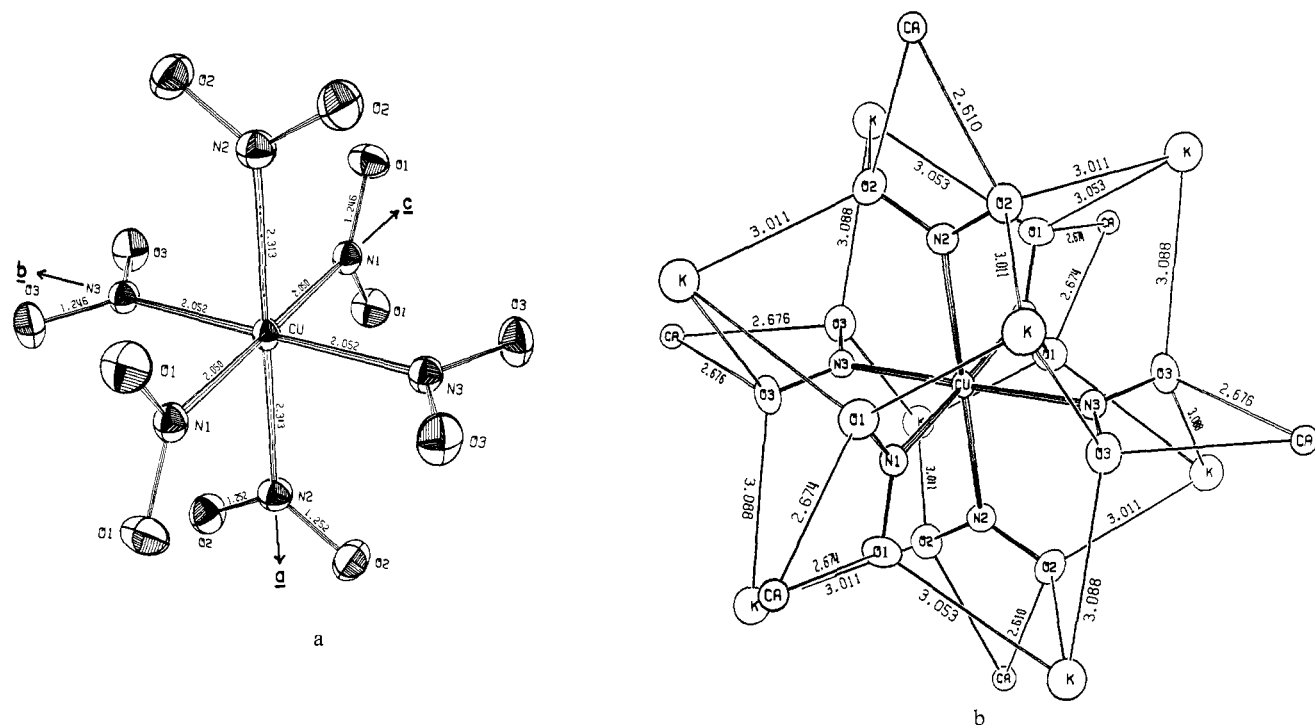
a

b

Figure 1. (a) Hexanitrocuprate(II) anion with bond distances. (b) Hexanitrocuprate(II) anion with nearest neighbor cations. The cell directions shown are for both figures. Both drawings made by ORTEP: C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
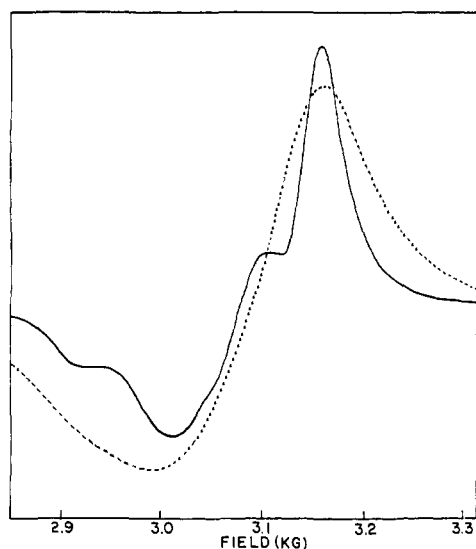

Figure 2. X-Band esr spectra for powdered $K_2CaCu(NO_2)_6$. Spectra were obtained with a Varian E-3 spectrometer at 9.125 GHz. The modulation frequency was 100 kHz: (——) 25° spectrum; (- - -) 175° spectrum.

deviation of the bond distances and bond angles are 0.001 Å and 0.1°, respectively. The crystallographic site symmetry for Cu(II) is D_{2h} (*mmm*) but two of the three pairs of Cu–N distances are equal within experimental error. This gives Cu(II) a tetragonal environment with a bond length difference of 0.26 Å between the long pair of Cu–N bonds and the two short pairs. An approximate threefold axis not required by the space group relates the three crystallographically independent nitrite ligands. This orientation of the nitrite groups violates the tetragonal symmetry of the CuN_6 configuration and is, in fact, the only signi-

ficant departure from tetragonal symmetry in the crystal.

The Ca(II) and K(I) cations each have 12 nearly equidistant oxygen atom neighbors. The Ca(II) coordination sphere includes six bidentate NO_2 groups. The Ca(II)–O distances for the NO_2 groups participating in the short and long Cu–N bonds are 2.675 and 2.610 Å, respectively. Each of the 12 oxygen atoms coordinated to K(I) is from a different NO_2 group. The K(I)–O distances average 3.071 Å for the oxygen atoms associated with the short Cu–NO_2 bonds and 3.011 Å for the long Cu–NO_2 bonds. Each oxygen atom is associated with one Ca(II) and two K(I) cations.

The thermal parameters for the nitrogen atoms (shown in Table III as root mean square vibration amplitudes) tend to indicate less motion along the Cu–N bonds and greater motion perpendicular to them, a situation often found with fairly rigid coordination groups. This contrasts with other structures which are expected to show Jahn–Teller distortions but which have all six metal bonds crystallographically equivalent. For example, the nitrogen atoms in cubic K_2CuPb- $(NO_2)_6$ have significantly greater root mean square vibration amplitudes along the Cu–N bonds.[2] Cullen and Lingafelter cite this observation as evidence that the expected tetragonal symmetry of the CuN_6 group is obscured either by a time average or a space average over bonds with tetragonal symmetry. It is clear that the averaging of two bonds of one length and a third bond of a different length would give octahedral symmetry with an apparent intermediate bond length and a thermal ellipsoid elongated in the bond direction.

The $K_2PbCu(NO_2)_6$ crystals are known to undergo a *reversible* phase transformation to a lower symmetry form below 280°K.[11,13] Precession photographs of single crystals at or below −35° show several ortho-

Table III. Root Mean Square Displacements (Å) for Principal Axes of Thermal Ellipsoids

| Atom | Crystal axis | | |
	a	b	c
Cu(II)	0.1259 (5)	0.1047 (5)	0.1024 (5)
Ca(II)	0.1220 (7)	0.1182 (7)	0.1212 (6)
K(I)	0.1774 (5)	0.1672 (5)	0.1722 (4)
N(1)	0.140 (2)	0.120 (2)	0.122 (2)
N(2)	0.132 (2)	0.142 (2)	0.140 (2)
N(3)	0.130 (2)	0.120 (2)	0.128 (2)
O(1)	0.166 (1)[a]	0.178 (1)	0.126 (1)[a]
O(2)	0.163 (1)[a]	0.133 (1)[a]	0.184 (1)
O(3)	0.191 (1)	0.153 (1)[a]	0.120 (1)[a]

[a] Not along the crystal axis.

rhombic lattices[24] and in fact are very similar to photographs of the multilattice $K_2CaCu(NO_2)_6$ crystals at room temperature. This observation suggested that the $K_2CaCu(NO_2)_6$ structure might transform to a cubic lattice at elevated temperatures. The esr spectrum of powdered $K_2CaCu(NO_2)_6$ at 180° (Figure 2) is close to isotropic which indicates a transformation to a cubic lattice does occur. The significantly greater stability of the Ca(II)-containing crystals, as compared to those containing Pb(II), raises the question of what properties the Pb(II) ion confers on the crystal and perhaps on the $[Cu(NO_2)_6]^{4-}$ ion to destabilize the orthorhombic form.

An X-ray analysis of the $K_2PbCu(NO_2)_6$ crystals at 190°K is now in progress. Preliminary results, including the orthorhombic cell constants, which are $a = 10.72$ (1), $b = 10.74$ (1), and $c = 10.51$ Å(1) , support the suggestion that the CuN_6 configuration in this crystal is compressed tetragonal. These lattice parameters are

in excellent agreement with those reported by Harrowfield and Pilbrow for the powder at 267°K ($a = 10.72$ and $c = 10.50$ Å).[13]

Although the present structure results provide additional experimental evidence for the dynamic–static Jahn–Teller effect, the ability of Pb(II) to stabilize the cubic lattice is still not explained. Hathaway and Slade[25] have attributed the stabilizing effect of Pb(II) (as compared to Ca(II) or Ba(II)) to a lead–oxygen bonding interaction caused by the higher polarizing ability and greater reducing power of Pb(II). Electron transfer spectral studies[26] of hexanitrometalate salts are consistent with electron transfer from Pb(II) to either NO_2^- or Cu(II). Although the N–O bond length for the lead salt is slightly longer (Table II), the differences are not significant in view of the suggested disorder in the lead salt. Refinement of the $K_2PbCu(NO_2)_6$ structure at low temperature may shed some light on this question.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6606.

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