

## Electron density distribution in potassium *bis*-(carbonato)cuprate(II)

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**Abstract.** The electron density distribution in potassium *bis*-(carbonato)cuprate(II) has been analyzed using x-ray diffraction data from an earlier structure determination. While the copper-ligand geometry is close to square planar the deformation density near the metal is strongly asymmetric. There are local maxima near the copper atom along the line of the Cu-K vectors. These resemble features found in corresponding regions in normal length metal-metal bonds. The observation is consistent with the long range nature of the Coulomb potential associated with the potassium ion.

**Keywords.** Coulomb potential; long range force; electron density deformation.

### 1. Introduction

The Coulomb potential is slowly varying at long range. For a random assembly of charges with the same sign long range interactions make a dominant contribution to the total energy because of their number. Such terms are relatively unimportant in crystalline materials because macroscopically matter is electrically neutral.

Chemical bonding refers to the equilibrium resulting from the static interaction between neutral atoms in close proximity. The overlapping of charge clouds alters the balance between attractive and repulsive forces to give a net attractive term which dominates the energy. The overlap contributions decrease rapidly with increasing internuclear separation.

The bonding interaction perturbs the atomic electron density distribution and the consequent displaced charge interacts *via* the Coulomb potential with other more distant neighbouring atoms. It is sometimes believed that the latter effect on the electron density should be far smaller than the first; this assumption is not consistent with the different ranges over which the contributing forces are effective. This consideration is important for example in the choice of basis functions for crystal orbital calculations and for the interpretation of deformation densities. To demonstrate the relative significance of the long range of the Coulomb potential the deformation density in a crystal structure in which the long range forces can be easily visualized has been examined. The crystal structure of potassium *bis*-(carbonato)cuprate(II),  $K_2Cu(CO_3)_2$ , was reported by Farrand *et al* (1980). It contains alkali metal atoms interacting at medium range with oxygen atoms and at longer range with a highly polarizable transition metal atom. A preliminary examination of the electron density distribution was made by Figgis *et al* (1981).

### 2. Experimental

The data from the original structural study were used in the present investigation. The intensities were corrected for absorption using the program ABCOR and reduced to

1693 independent observations. The refinement in the earlier charge density study was based on  $I$  rather than  $F$  to eliminate the bias caused by setting to zero those observations for which the experimentally determined intensities were negative. This is not appropriate when the optimum values of the structure factor moduli and their associated errors are required for the calculation of reliable difference densities (French and Wilson 1978). To treat the negative observations correctly the intensities and their estimated standard deviations were modified using a Bayesian statistics approach which combines prior knowledge of the non-negativity of the true intensities with the intensity distribution determined from the data set.

The positional and thermal parameters were redetermined in a weighted, full matrix least squares refinement using all 1693 independent reflections. The form factors for  $K^+$ , Cu, C and O by Cromer and Mann (1968) and their respective real and imaginary anomalous dispersion corrections (Cromer and Liberman 1970) were used and the data were weighted by  $1/\sigma^2(F)$ . The refinement converged giving the agreement factors shown in table 1. The final structure parameters are listed in table 2. Interatomic distances and angles are given in table 3.

### 3. Structure

The structure of  $K_2Cu(CO_3)_2$  has been discussed by Farrand *et al* (1980). It consists of almost square planar copper-ligand oxygen moieties linked in a polymeric array by bridging carbonate ligands. The potassium cations are interspersed through the array. Although each copper atom is on a crystallographic two-fold rotation axis the geometrical structure exhibits local four-fold symmetry about this site. The angles between the Cu-O(1) and Cu-O(2) vectors are  $88.56(6)$  and  $92.00(6)^\circ$  and the bond lengths are  $1.934(1)$  and  $1.929(1)$  Å respectively. The copper-ligand atom chromophore deviates slightly from planarity in a tetrahedral sense with the copper atom lying  $0.06$  Å above and each symmetry related pair of oxygens lying  $0.14$  Å above and  $0.16$  Å below the least squares plane through these five atoms.

The geometry of each bridging carbonate anion differs significantly from trigonal

**Table 1.** Experimental and refinement data.

Space Group	Fdd2
Cell Dimensions	a
	b
	c
	U
Z	8
$\mu(\text{MoK}_\alpha)$	$47 \text{ cm}^{-1}$
Diffractometer	Syntex P2 <sub>1</sub>
Monochromator	Graphite
Maximum $2\theta$	$100^\circ$
Independent reflections	1693
Reflections used	1693
Final R factor (on F)	0.035
Final weighted R factor (on F)	0.026
Weights used	$1/\sigma^2(F_0)$

**Table 2.** Final atomic positional parameters expressed in fractional coordinates with estimated standard deviations in parentheses.

	$x/a$	$y/b$	$z/c$
Cu	0(0)	0(0)	0(0)
K	0.57808(4)	0.20005(2)	0.19615(9)
O(1)	0.08278(11)	0.09545(7)	0.01308(29)
O(2)	0.10135(11)	0.19980(7)	0.21335(35)
O(3)	0.05979(13)	0.08876(9)	0.37189(31)
C	0.08180(14)	0.12671(9)	0.20509(39)

**Table 3.** Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.

<i>Bond distances</i>	
Cu-O(1)	1.9343(13)
Cu-O(2) <sup>i</sup>	1.9290(13)
C-O(1)	1.3042(29)
C-O(2)	1.3108(20)
C-O(3)	1.2514(28)
<i>Interatomic distances</i>	
Cu-K <sup>ii</sup>	3.8649(11)
Cu-K <sup>iii</sup>	3.4892(9)
Cu-K <sup>iv</sup>	4.0315(11)
<i>Bond angles</i>	
O(1)-Cu-O(2) <sup>i</sup>	88.56(6)
O(1)-Cu-O(2) <sup>ii</sup>	92.00(6)
O(1)-C-O(2)	116.77(20)
O(1)-C-O(3)	121.22(16)
O(2)-C-O(3)	121.98(22)

i.  $(1/4 - x, -1/4 + y, -1/4 + z)$  ii.  $(-1/4 + x, 1/4 - y, -1/4 + z)$   
 iii.  $(3/4 - x, -1/4 + y, 1/4 + z)$  iv.  $(3/4 - x, -1/4 + y, -3/4 + z)$

planar. The bridging bonds, C-O(1) and C-O(2), are elongated relative to the free C-O(3) bond and the O(1)-C-O(2) angle is compressed from the ideal  $120^\circ$  to  $116.8(2)^\circ$ .

One pair of K cations, related by the two-fold axis, lies only 0.27 Å from the Cu-ligand oxygen plane, with the Cu-K vectors of length 3.865 Å directed midway between the respective Cu-O(1) and Cu-O(2) bonds. Four other K cations surrounding the same copper atom (two above at 3.489 Å and two below at 4.032 Å) form with the copper atom a plane perpendicular to the Cu-ligand oxygen plane. All these distances between Cu and K are short enough that the possibility of significant electrostatic interactions between Cu and K must be considered.

#### 4. Electron density

The difference density section in the Cu-ligand oxygen plane is shown in figure 1. While the immediate structural environment of Cu has pseudo four-fold symmetry the electron density distribution shows little trace of such symmetry. There are two pairs of

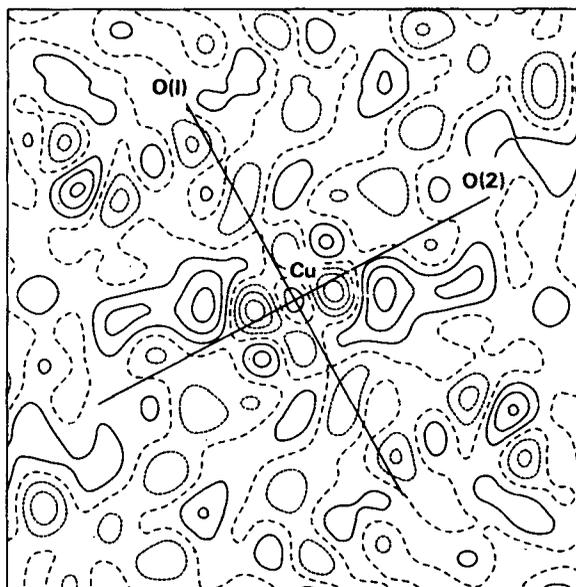


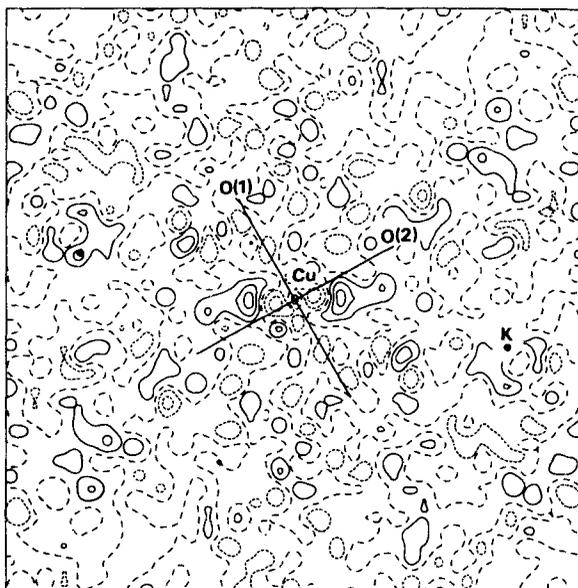
Figure 1. Residual electron density in the section containing Cu, O(1) and O(2). Contour interval is  $0.2 \text{ e}\text{\AA}^{-3}$

local maxima within  $0.8 \text{ \AA}$  of the copper atom lying between the Cu-O(1) and Cu-O(2) bonds. Each member of a pair is related to the other by the two-fold axis but the pairs do not resemble each other topologically. These features are not consistent with the nearest neighbour geometry.

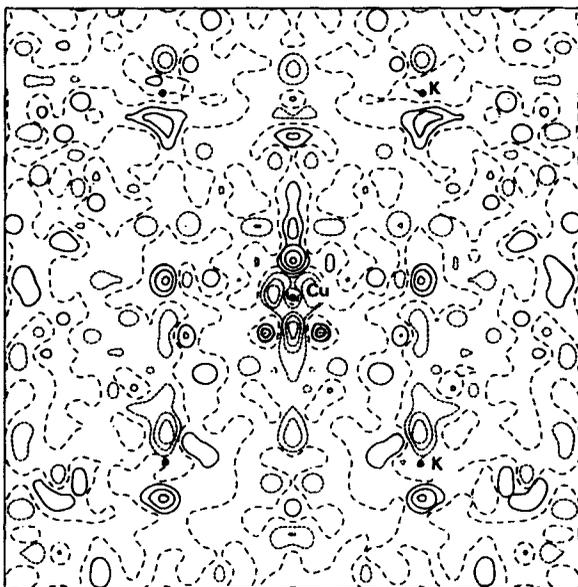
The difference map features can be accounted for in qualitative terms if the effects of next-to-nearest neighbours are considered. In figure 2 the difference density in the same plane extended to  $5 \text{ \AA}$  from the copper atom is shown. The broader pair of peaks near the copper are directed towards the approximately in-plane K atoms. The electron-deficient regions near the copper atom are rotated approximately  $15^\circ$  from the respective copper-oxygen bonds.

Figure 3 shows the section through the four potassium cations above and below the Cu-ligand oxygen plane. Sharp maxima lie directly along the shortest Cu-K vectors, with more diffuse regions of excess density along the longest Cu-K vectors. Regions of electron density excess near the potassium atoms are directed approximately towards the copper atom.

Although the results must be viewed with caution because of the phase errors associated with the structure factors of this non-centrosymmetric structure, the features in the difference maps are consistent with a medium range electrostatic interaction between the copper and alkali metal atoms. The significance of this effect has been reinforced by the results of a charge density study of the centrosymmetric sodium analogue,  $\text{Na}_2\text{Cu}(\text{CO}_3)_2$  (Maslen *et al* 1983). Features in that analysis, which are not hampered by potential difficulties of phasing, are similar to those described above. In  $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ , the effects of next-to-nearest neighbours on the polarization of the metal electron density is observed on a number of difference density sections.



**Figure 2.** Residual density in the section containing Cu, O(1) and O(2) extended to a distance of at least 5.0 Å from Cu. Contour interval is  $0.2 \text{ e}\text{\AA}^{-3}$ .



**Figure 3.** Residual density in section perpendicular to the plane in figure 1 containing the two-fold axis and the Cu and four K atoms. Contour interval is  $0.2 \text{ e}\text{\AA}^{-3}$ .

## 5. Conclusions

It has been shown that residual density near transition metal atoms for near-to-ideal structures can be described in terms of the effects of the nearest neighbour geometry (Marumo *et al* 1974). In the present case, however, such a procedure is inadequate and the interpretation must be extended to correlate the density features with next-to-nearest neighbour interactions. These features resemble those observed in normal length bonds between metal atoms (Wang and Coppens 1976; Mitschler *et al* 1978). This suggests that the Cu-K interaction might be regarded as a weak metal-metal bond. Ito and Higashi (1983) have recently reported similar features along the Al-Al vectors in  $\text{LiAlB}_{14}$ . The Al-Al distance in that structure is 2.92 Å.

The assertion that in these cases nearest neighbour and next-to-nearest neighbour interactions lead to effects of comparable magnitude reflects the slowly varying nature of the Coulomb potential. It is therefore important always to consider all interactions in the interpretation of residual density maps.

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