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A New Type of Copper Complex as found in the Crystal Structure of Cupric Acetate, $Cu_2(CH_3COO)_4 . 2H_2O$

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Crystals of cupric acetate are monoclinic with space group $C2/c$. The unit cell, of dimensions $a = 13{\cdot}15$, $b = 8{\cdot}52$, $c = 13{\cdot}90$ Å, $\beta = 117° 0'$, contains four $Cu_2(CH_3COO)_4.2H_2O$ molecules. The symmetry centre of this binuclear molecule coincides with a symmetry centre of the $C2/c$ space group.

Projections of the structure on three crystallographic planes are given. The four acetate groups in a single molecule are separately planar and have normal bond distances and angles. The way in which they bridge the two copper atoms in a molecule is illustrated.

The most striking feature of this sixfold co-ordinated copper complex is the close approach of 2·64 Å between the two copper atoms. In this unusual configuration each of the two copper atoms forms, in addition to four co-planar bonds to four oxygen atoms, also a bond to a copper atom and to a water molecule. The nature of these bonds is open to speculation.

Hydrogen bonds appear to be mainly responsible for the forces between molecules. The way in which the molecules are packed in the structure is illustrated.

1. Introduction

While investigating the crystal structure of chromous acetate it was noticed that its unit-cell dimensions and space group are closely related to corresponding data for cupric acetate as determined by Hull (1938). For these reasons, together with the experimental difficulties involved in handling the unstable chromous compound, it appeared likely that a preliminary X-ray examination of cupric acetate, which is very stable, might provide valuable information as regards the structure of chromous acetate. Subsequent experiments revealed some rather unexpected features and it was accordingly decided to make a detailed determination of the structure of cupric acetate.

2. Crystal data

The crystallography of cupric acetate has been described by Brooke (1823), Schabus (1855), Groth (1910) and Hull (1938). A chemical analysis of the material used during this investigation gave the following results:

	Theoretical	Determined
Cu	31·84	31·50
C	24·05	24·20
H	4·05	4·15
Acetic acid	60·1	59·9

The unit-cell dimensions, as determined from rotation and Weissenberg photographs, are given below. These values are in good agreement with those obtained by Hull (1938).

	a (Å)	b (Å)	c (Å)	β
	13·15	8·52	13·90	117° 0′
Hull's values	13·176	8·463	13·89	117° 6′

The crystals are dark green in colour and comparatively hard. In the literature they are classified as monoclinic holohedral. Systematic extinctions occur for hkl with $h+k$ odd, $h0l$ with h odd and l odd and $0k0$ with k odd. The space group is therefore either Cc or $C2/c$. The crystals were tested for pyro-electricity following methods described by Bunn (1946). The results were negative although other crystals belonging to the non-centrosymmetrical classes, when tested in the same way, gave positive results. These experiments, although not conclusive, at least do not contradict the $C2/c$ space group. The successful structural analysis of this compound probably gives the most direct evidence that the crystals belong to the $C2/c$ space group.*

The density, as determined by flotation, is 1·92 g.cm.$^{-3}$. Assuming four $Cu_2(CH_3COO)_4.2H_2O$ formula units in a cell with the above dimensions, the calculated density is 1·92 g.cm.$^{-3}$.

Weissenberg photographs of several layers were taken with filtered Mo $K\alpha$ and Cu $K\alpha$ radiation using the multiple-film technique. From these films intensities of the reflexions were estimated visually by comparing them with a standard set of spots of proportionately increasing exposure times. Lorentz and polarization corrections were made according to Kaan & Cole (1949). Absorption and extinction effects were neglected in view of the small size of the crystals used. By measuring a number of suitable spectra on a Geiger-counter X-ray spectrometer, using methods similar to those of Lonsdale (1948) and Cochran (1950),

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* *Note added in proof* 13 *January* 1953.—A subsequent statistical $N(z)$ test, using all the hkl spectra, confirms a centrosymmetrical space group.

all the relevant intensities were expressed on an approximately absolute scale. The conversion factor 7·9, obtained in this way, agreed well with the factor 8·0 which was calculated according to methods described by Wilson (1942) and Harker (1948). This agreement may, however, be largely fortuitous.

3. Preliminary estimate of the structure

The optical properties of cupric acetate have been investigated by Bolland (1910). No useful information as regards a likely atomic arrangement could, however, be derived from these data. Since the general point position in the $C2/c$ space group is eightfold and because there are four $Cu_2(CH_3COO)_4.2\,H_2O$ formula units in the unit cell, none of the atoms occupy special positions. Recourse was therefore taken to direct methods, not involving a knowledge of the phases of the spectra, in order to locate the position of the heavy copper atom in the structure. The following projections and sections were accordingly evaluated: $P(u,w)$, $P(u,v)$, $P(v,w)$, $P(u,o,w)$, $P(o,v,\frac{1}{2}c)$ and $P(u,\frac{1}{2}b,w)$. For reasons of space only the last two sections are shown in Figs. 1 and 2 respectively.

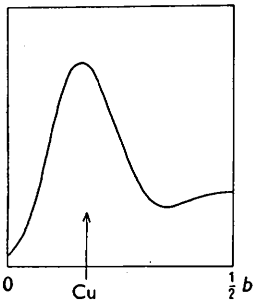

Fig. 1. Harker section $P(0, v, \frac{1}{2}c)$. The final copper position is indicated.

The interpretation of Fig. 1, which gives the distance of a copper atom from the glide plane, is both obvious and unique. The interpretation of Fig. 2 is by no means straightforward since in this section there appear, in addition to a large number of smaller peaks, three main peaks (I, II, III) of very nearly equal intensity, together with a fourth peak (IV) only slightly smaller in intensity.

Applying the criterion of maximum separation between copper atoms, the possible positions of the copper atom as suggested by these four main peaks were tried in the following order: III, IV, I and II. In an effort to find correlation between the above-mentioned Patterson and Harker syntheses, together with results obtained from a preliminary Fourier analysis, peak I was finally found to represent the Cu–Cu vector. The three remaining heavy peaks in Fig. 2 could only be explained once the structure was known. Referring to Fig. 7, they are shown to represent the following non-Harker vectors:

Peak II: Cu(5·00)–O(0·43), Cu(3·50)–O(−0·85) and C(4·04)–C(−0·07) twice.

Peak III: O(−2·13)–O(2·13), C(4·04)–C(−0·07) and C(4·18)–C(−0·21).

Peak IV: Cu(0·75)–O(5·17) and H_2O(2·55)–O(−2·13).

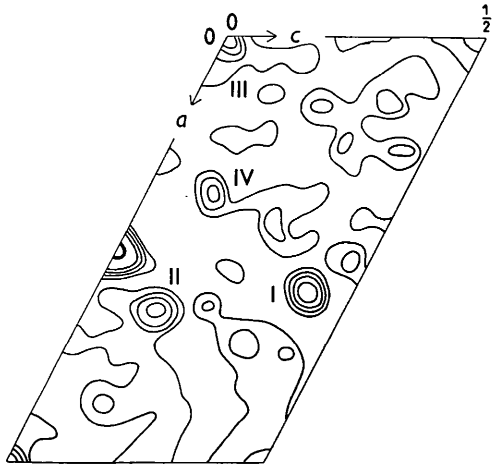

Fig. 2. Harker section $P(u, \frac{1}{2}b, w)$. Contours are drawn at arbitrary levels; the heavy contour represents a much higher level.

The values in brackets are shown in the diagram and give the y coordinates of the atoms mentioned above.

4. Projections of the structure on three crystallographic planes

Combining the observed $F(h0l)$ values with the phases of the copper atom as calculated from its position derived in § 3 above, the $\sigma(x,z)$ projection was evaluated first as it promised the best resolution. From this preliminary projection it was finally established that the true repeat unit is $Cu_2(CH_3COO)_4.2\,H_2O$ and that the symmetry centre of this unit coincides with a symmetry centre of the $C2/c$ space group. Phase calculations of the $F(h0l)$ factors were then extended to include all the atoms, using the following temperature-corrected atomic scattering factors. For carbon the values obtained by Robertson (1935) were used. For oxygen the values of James & Brindley (1931) were reduced proportionately. For copper the f values given by Thomas–Fermi were multiplied by the Debye–Waller temperature factor $\exp[-0{\cdot}87\,(\sin\theta/\lambda)^2]$.

The final $\sigma(x,z)$ projection is shown in Fig. 3 and the final structure factors are tabulated in Table 1. The agreement between the observed and calculated values is good and leads to an R factor of 0·21 when the absent spectra are not taken into account. Because of the relatively high and fluctuating background in this and other projections, the first contour drawn is at the 6 e.Å^{-2} level.

The relation of two of the four acetate groups to the two copper atoms in a molecule is clearly visible

Table 1. *Observed and calculated structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	122	+193	$60\bar{6}$	124	−139	$16,0,\overline{14}$	41	−46
400	43	−51	$60\bar{8}$	56	−76	$16,0,\overline{16}$	31	−48
600	67	−35	$6,0,\overline{10}$	62	+28	$18,0,\bar{2}$	38	+52
800	111	−91	$6,0,\overline{12}$	63	+38	$18,0,\bar{4}$	36	+49
10,0,0	45	−47	$6,0,\overline{14}$	74	+65	$20,0,\bar{2}$	27	+29
12,0,0	50	−63	$6,0,\overline{16}$	87	+81			
14,0,0	23	−27	$6,0,\overline{18}$	34	+39	021	48	−48
020	97	+115	802	45	−24	041	15	−15
040	53	−58	804	< 20	−24	061	24	−21
060	160	−163	806	90	+74	081	43	+28
080	24	− 2	808	102	+104	0,10,1	29	+21
0,10,0	33	+58	8,0,10	46	+61	022	57	−45
002	139	+219	8,0,12	25	+45	042	83	−88
004	10	− 2	$80\bar{2}$	108	−95	062	148	−143
006	< 14	−23	$80\bar{4}$	41	−58	082	< 13	− 4
008	108	−90	$80\bar{6}$	38	−60	0,10,2	24	+39
0,0,10	72	−53	$80\bar{8}$	31	− 4	023	79	−104
0,0,12	73	−78	$8,0,\overline{10}$	48	+51	043	68	−82
0,0,14	53	−59	$8,0,\overline{12}$	86	+93	063	35	−32
0,0,16	23	−17	$8,0,\overline{14}$	121	+96	083	55	+47
202	202	+310	$8,0,\overline{16}$	81	+52	0,10,3	31	+33
204	200	+272	10,0,2	66	−65	024	< 10	+13
206	79	+50	10,0,4	44	−37	044	36	+23
208	< 19	− 2	10,0,6	< 24	+ 2	064	54	−82
2,0,10	74	−57	10,0,8	< 26	+22	084	< 14	+ 2
2,0,12	93	−76	10,0,10	52	+64	0,10,4	10	+ 6
2,0,14	64	−62	10,0,12	38	+52	025	86	−98
2,0,16	< 26	− 37	$10,0,\bar{2}$	118	−126	045	105	−105
$20\bar{2}$	113	+138	$10,0,\bar{4}$	48	−49	065	23	+35
$20\bar{4}$	108	−114	$10,0,\bar{6}$	48	+43	085	64	+75
$20\bar{6}$	54	− 35	$10,0,\bar{8}$	53	+48	0,10,5	45	+45
$20\bar{8}$	131	−106	$10,0,\overline{10}$	114	+112	026	28	− 8
$2,0,\overline{10}$	152	−141	$10,0,\overline{12}$	87	+82	046	88	+69
$2,0,\overline{12}$	< 21	−24	$10,0,\overline{14}$	41	+41	066	27	+29
$2,0,\overline{14}$	< 23	−20	$10,0,\overline{16}$	< 24	+11	086	< 15	−10
$2,0,\overline{16}$	< 25	+13	12,0,2	80	−75	0,10,6	20	−18
$2,0,\overline{18}$	36	+43	12,0,4	45	−42	027	116	−137
$2,0,\overline{20}$	27	+43	$12,0,\bar{2}$	< 20	0	047	116	−113
402	184	+215	$12,0,\bar{4}$	< 20	+ 3	067	< 13	+25
404	215	+253	$12,0,\bar{6}$	69	+69	087	71	+74
406	155	+152	$12,0,\bar{8}$	96	+89	028	89	−79
408	51	+31	$12,0,\overline{10}$	95	+81	048	56	+23
4,0,10	< 21	0	$12,0,\overline{12}$	123	+71	068	55	+48
4,0,12	42	−33	$12,0,\overline{14}$	< 23	−10	088	< 14	+ 5
4,0,14	23	−51	$12,0,\overline{16}$	32	−30	029	76	−85
4,0,16	38	−44	$12,0,\overline{18}$	24	−34	049	47	−44
$40\bar{2}$	116	−114	$12,0,\overline{20}$	36	−48	069	< 14	−14
$40\bar{4}$	57	−45	14,0,2	23	−47	089	31	+43
$40\bar{6}$	135	−130	$14,0,\bar{2}$	22	+26	0,2,10	21	−14
$40\bar{8}$	44	−54	$14,0,\bar{4}$	59	+70	0,4,10	39	+42
$4,0,\overline{10}$	32	−70	$14,0,\bar{6}$	77	+72	0,6,10	68	+67
$4,0,\overline{12}$	< 20	−40	$14,0,\bar{8}$	113	+88	0,8,10	23	+27
$4,0,\overline{14}$	49	+41	$14,0,\overline{10}$	42	+37	0,2,11	< 14	− 3
$4,0,\overline{16}$	54	+52	$14,0,\overline{12}$	< 23	−11	0,4,11	27	+ 5
$4,0,\overline{18}$	69	+65	$14,0,\overline{14}$	22	−13	0,6,11	< 15	+ 6
$4,0,\overline{20}$	38	+42	$14,0,\overline{16}$	34	−48	0,2,12	27	−34
602	<15	− 9	$14,0,\overline{18}$	25	−51	0,4,12	24	+30
604	113	+98	$14,0,\overline{20}$	26	−42	0,6,12	47	+51
606	137	+123	$16,0,\bar{2}$	41	+45	0,2,13	35	+35
608	143	+125	$16,0,\bar{4}$	56	+60	0,4,13	21	+16
6,0,10	44	+54	$16,0,\bar{6}$	55	+65	0,2,14	42	−37
6,0,12	< 25	− 7	$16,0,\bar{8}$	39	+35	0,4,14	22	+38
$60\bar{2}$	40	−30	$16,0,\overline{10}$	< 25	+ 4	0,2,15	36	+35
$60\bar{4}$	133	−121	$16,0,\overline{12}$	40	−38			

in this projection. In order to obtain further information as regards the positions of the remaining two acetate groups, the structure was projected on the (101) plane. For this synthesis the signs of the relevant structure factors were calculated for the copper atom only, and the F factors are therefore not included in Table 1. The projection of the structure on the (101) plane is shown in Fig. 4. This diagram shows clearly the positions of the two acetate groups under consideration.

Although the general features of the molecule are apparent from these two projections, the structure was also projected on the *b c* plane with a view of obtaining better resolution in the case of certain atoms and hence more accurate parameters. Lipson & Beevers strips were again used and the final $\sigma(y, z)$ projection is shown in Fig. 5. Again excluding absent spectra, an *R* factor of 0·20 was found between the observed and calculated structure factors which are listed in Table 1.

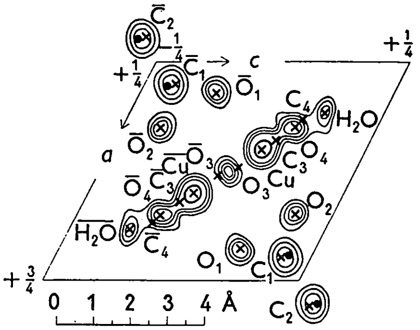

Fig. 3. Electron density projected on the *a c* plane. Contours are drawn at intervals of 2 e.Å^{-2}; the outer line is the six-electron contour. The heavy lines are the 50 e.Å^{-2} contours. Atoms marked by crosses belong to a single molecule. Atoms derived from symmetry are shown as black dots.

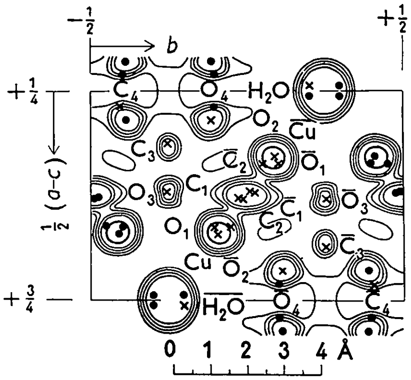

Fig. 4. Electron density projected on the (101) plane. The contours and the marking of atoms are as for Fig. 3.

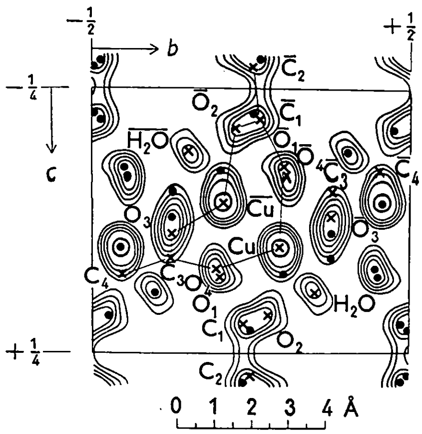

Fig. 5. Electron density projected on the *b c* plane. Contours and labelling of atoms are as for Fig. 3.

In all these projections the origin was taken as in *International Tables* for the *C*2/*c* space group.

5. Description of the molecule

Because of considerable overlapping in all three electron-density projections, the final parameters (Table 2) were estimated from the best positions consistent with all three projections.

Table 2. *Final parameters*

Atom	x/a	y/b	z/c
Cu	0·450	0·088	0·044
O_1	0·677	−0·100	0·101
O_2	0·598	0·050	0·175
O_3	0·492	−0·250	0·017
O_4	0·400	−0·108	0·087
H_2O	0·367	0·200	0·132
C_1	0·697	−0·025	0·192
C_2	0·807	−0·008	0·296
C_3	0·427	−0·250	0·063
C_4	0·385	−0·400	0·095

The distances and angles in a molecule, as calculated from the parameters given in Table 2, are tabulated in Table 3, and in Fig. 6 a sketch of the binuclear molecule is shown. The six nearest neighbours of a copper atom are comprised of four oxygen atoms belonging to four different acetate groups, a copper atom and a water molecule. Six such atoms form a distorted octahedral configuration about each of the two copper atoms. Within the errors of experiment the four acetate groups belonging to a single molecule are separately planar. The angles between the planes of adjacent acetate groups are 83° and 97°. The dimensions of the acetate groups conform with those determined for basic beryllium acetate by Pauling & Sherman (1934) and for sodium uranyl acetate by Fankuchen (1935).

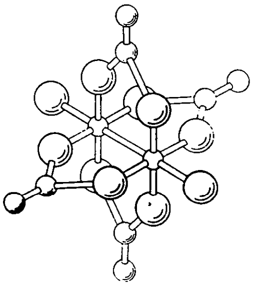

Fig. 6. A sketch of the cupric acetate molecule. The two small central circles are copper atoms.

The Cu–O distances agree well with corresponding distances (1·95 Å) found in CuO by Tunell, Posnjak & Ksanda (1935) and also with the Cr–O distances (1·96 Å) found by van Niekerk & Schoening (1951,

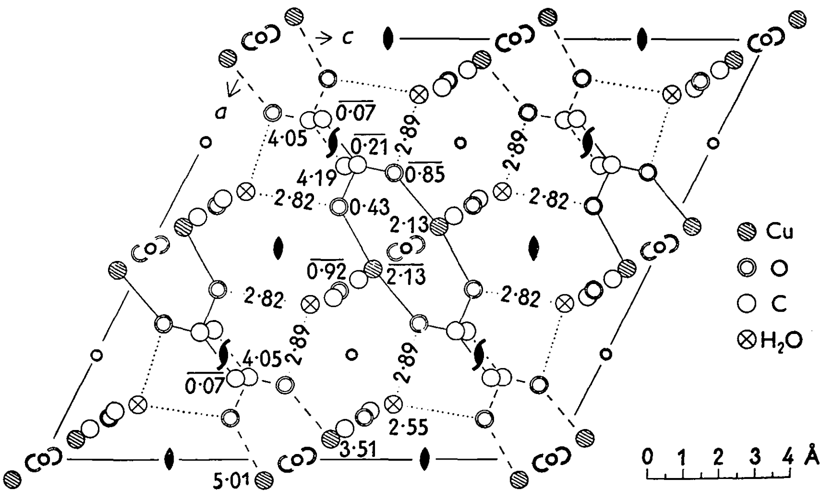

Fig. 7. Projection of the structure on the $a\,c$ plane. Atoms joined by broken lines lie $\frac{1}{2}b$ above and below those joined by full lines. Dotted lines show hydrogen bond links. The y coordinates of certain atoms are shown.

1952) in a number of chromic complexes. The two water molecules and the two copper atoms in a molecule are collinear.

Table 3. *Dimensions of molecule*

All distances are in Ångström units and all angles in degrees

Atoms		Mean
$\mathrm{Cu{-}\overline{Cu}}$	2·64	—
$\mathrm{Cu{-}H_2O}$	2·20	—
$\mathrm{\overline{Cu}{-}O_1}$	1·96	1·97
$\mathrm{Cu{-}O_2}$	1·99	
$\mathrm{\overline{Cu}{-}O_3}$	1·95	
$\mathrm{Cu{-}O_4}$	1·98	
$\mathrm{O_1{-}O_2}$	2·17	2·20
$\mathrm{O_3{-}O_4}$	2·23	
$\mathrm{O_1{-}C_1}$	1·33	1·33
$\mathrm{O_2{-}C_1}$	1·36	
$\mathrm{O_3{-}C_3}$	1·29	
$\mathrm{O_4{-}C_3}$	1·34	
$\mathrm{C_1{-}C_2}$	1·52	1·52
$\mathrm{C_3{-}C_4}$	1·52	
$\mathrm{O_1{-}C_1{-}O_2}$	108°	112°
$\mathrm{O_3{-}\overline{C_3}{-}O_4}$	116°	
$\mathrm{Cu{-}\overline{Cu}{-}O}$	—	83°

6. Discussion of the structure

The way in which the cupric acetate molecules are arranged in the structure and the bonding between them is illustrated in Fig. 7. In this diagram the contents of slightly more than one unit cell, when projected on the $a\,c$ plane, is shown. Apart from van der Waals forces, each molecule is linked by eight hydrogen bonds (2·82 and 2·89 Å) to four neighbouring molecules at different levels. In the diagram these bonds are shown as dotted lines.

Considering the configuration of individual complex molecules it is interesting to note that, to the knowledge of the authors, such a configuration has not been previously observed. From chemical reasoning Werner (1910) has shown that an acetate group can attach itself to two different metal atoms to form a bridge across them, and such a bridged structure has been observed by Pauling & Sherman (1934) in basic beryllium acetate. In structures previously described, however, no direct bond between the central metal atoms has been observed, whereas the short Cu–Cu distance (2·64 Å) in cupric acetate indicates that such a bond may well exist in this structure.

Four oxygen atoms, arranged approximately on a square, form the nearest neighbours of a copper atom (1·97 Å). In this respect the co-ordination resembles that normally encountered in divalent copper compounds (Wells, 1949). Perpendicularly above and below the plane containing the four oxygen atoms lies a water molecule at a distance 2·20 Å and a copper atom at a distance 2·64 Å, thus completing the distorted octahedral configuration about each copper atom. Further evidence of the distortion in the molecule is to be seen by comparing the Cu–Cu distance (2·64 Å) and the O–O distance for one acetate group (2·20 Å).

Until further information becomes available no attempt will be made to explain the bonds in this unusual complex. For this purpose a systematic investigation of the acetates of the other transition elements has been started. Work now in progress strongly suggests that chromous acetate has a similar structure.

Note added in proof 13 *January* 1953.—After this paper had been accepted for publication, detailed magnetic measurements of cupric acetate were reported by Bleaney & Bowers (1952). These authors predict the existence of isolated pairs of copper ions coupled by exchange forces, with each copper ion bonded by four oxygen atoms in a plane. This is exactly the arrangement described in the present structure. Their z

direction (a principle axis of the crystalline electric field) corresponds in our case with the line joining the two copper ions in a molecule. This line makes an angle of 34·6° with the *a c* plane, and its projection on to the *a c* plane an angle of 32·5° with the *c* axis. The corresponding values given by Bleaney & Bowers for their *z* direction are 33° and 33°.

The authors further discuss the question as to whether the interaction between the copper ions is of a direct nature (Cu–Cu distance 2 Å), or of Kramers's super-exchange type acting through intermediate oxygen atoms (Cu–Cu distance 4 Å). Whereas they seem to favour the latter type of interaction, the the structure described in this paper undoubtedly indicates direct interaction between the copper ions (Cu–Cu distance 2·64 Å).

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Vibrational Modifications of the Electron Distribution in Molecular Crystals. I. The Density in a Vibrating Carbon Atom

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The electron density derived from measurements of the Laue scattering of X-rays by a crystal is shown to be the density in the stationary crystal averaged over all possible displaced configurations of the atomic nuclei in thermal equilibrium together at the temperature of the experiment. The calculation of the mean electron distribution falls into two parts: in general the mean density in an atom is a function of the tensor formed by the mean square amplitudes and mean products of amplitudes of the atomic motion; for a particular crystal this tensor has to be calculated from the force constants and geometry.

In the present paper the mean density in a carbon atom is computed as a function of the r.m.s. amplitude of isotropic thermal motion. It is found that quite a small amplitude suffices to reduce the peak density considerably below the value in a stationary atom; on the other hand, the bridge density in a bond between two atoms is increased. At the amplitudes which occur in many molecular crystals at ordinary temperatures the distribution in an atom is nearly gaussian.

In Part II these results will be applied to the interpretation of some experimental distributions.

1. Introduction

Recently theoretical calculations of the electron distributions in some conjugated organic molecules have been made according to several different approximations: Klement (1951) has treated naphthalene by the valence-bond technique; March (1952) has applied both the molecular-orbital and the Thomas–Fermi methods to benzene. On the other hand, detailed electron-density contour maps derived from X-ray diffraction measurements on crystals of